

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing: 16 December 1999 (16.12.99)	
International application No.: PCT/JP98/02610	Applicant's or agent's file reference: P98-19
International filing date: 12 June 1998 (12.06.98)	Priority date:
Applicant: KAMIYAMA, Shiro et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International preliminary Examining Authority on:
22 September 1999 (22.09.99)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer: J. Zahra Telephone No.: (41-22) 338.83.38
---	---

PCT

EP

US

国際調査報告

(法8条、法施行規則第40、41条)

[PCT18条、PCT規則43、44]

出願人又は代理人 の書類記号 P98-19	今後の手続きについては、国際調査報告の送付通知様式(PCT/ISA/220) 及び下記5を参照すること。	
国際出願番号 PCT/JP98/02610	国際出願日 (日.月.年) 12.06.98	優先日 (日.月.年)
出願人(氏名又は名称) 住化エイビーエス・ラテックス株式会社		

国際調査機関が作成したこの国際調査報告を法施行規則第41条(PCT18条)の規定に従い出願人に送付する。
この写しは国際事務局にも送付される。

この国際調査報告は、全部で 3 ページである。

☐ この調査報告に引用された先行技術文献の写しも添付されている。

1. ☐ 請求の範囲の一部の調査ができない(第I欄参照)。

2. ☐ 発明の単一性が欠如している(第II欄参照)。

3. ☐ この国際出願は、ヌクレオチド及び/又はアミノ酸配列リストを含んでおり、次の配列リストに基づき国際調査を行った。

☐ この国際出願と共に提出されたもの

☐ 出願人がこの国際出願とは別に提出したもの

☐ しかし、出願時の国際出願の開示の範囲を越える事項を含まない旨を記載した書面が添付されていない

☐ この国際調査機関が書換えたもの

4. 発明の名称は ☒ 出願人が提出したものを承認する。

☐ 次に示すように国際調査機関が作成した。

5. 要約は ☒ 出願人が提出したものを承認する。

☐ 第III欄に示されているように、法施行規則第47条(PCT規則38.2(b))の規定により国際調査機関が作成した。出願人は、この国際調査報告の発送の日から1カ月以内にこの国際調査機関に意見を提出することができる。

6. 要約書とともに公表される図は、
第 図とする。 ☐ 出願人が示したとおりである。

☒ なし

☐ 出願人は図を示さなかった。

☐ 本図は発明の特徴を一層よく表している。

A. 発明の属する分野の分類 (国際特許分類 (IPC))

Int. Cl.⁸ C08L51/04, 77/12, 25/12, C08K5/42

B. 調査を行った分野

調査を行った最小限資料 (国際特許分類 (IPC))

Int. Cl.⁸ C08L1/00-101/10, C08K3/00-13/08

最小限資料以外の資料で調査を行った分野に含まれるもの

国際調査で使用した電子データベース (データベースの名称、調査に使用した用語)

C. 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
Y	J P, 4-337344, A (東レ株式会社) 25. 11月. 1992 (25. 11. 92), 特許請求の範囲 (ファミリーなし)	1-8
Y	J P, 8-253640, A (三井東圧化学株式会社) 1. 10月. 1996 (01. 10. 96), 特許請求の範囲, 【0024】 (ファミリーなし)	1-8
Y	J P, 8-48768, A (三洋化成工業株式会社) 20. 2月. 1996 (20. 02. 96), 特許請求の範囲, 【0031】 (ファミリーなし)	1-8

☒ C欄の続きにも文献が列挙されている。☐ パテントファミリーに関する別紙を参照。

* 引用文献のカテゴリー

「A」特に関連のある文献ではなく、一般的技術水準を示すもの

「E」先行文献ではあるが、国際出願日以後に公表されたもの

「L」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献 (理由を付す)

「O」口頭による開示、使用、展示等に言及する文献

「P」国際出願日前で、かつ優先権の主張の基礎となる出願

の日の後に公表された文献

「T」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの

「X」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの

「Y」特に関連のある文献であって、当該文献と他の1以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの

「&」同一パテントファミリー文献

国際調査を完了した日

24. 08. 98

国際調査報告の発送日

01.09.98

国際調査機関の名称及びあて先

日本国特許庁 (ISA/J P)

郵便番号 100-8915

東京都千代田区霞が関三丁目4番3号

特許庁審査官 (権限のある職員)

一色 由美子

印

4 J

7537

電話番号 03-3581-1101 内線 3458



C (続き) . 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
Y	J P, 8-81645, A (日本合成ゴム株式会社) 26. 3月. 1996 (26. 03. 96), 特許請求の範囲 (ファミリーなし)	1-8
Y	J P, 9-279024, A (三洋化成工業株式会社) 28. 10 月. 1997 (28. 10. 97), 特許請求の範囲, 【000 1】 (ファミリーなし)	1-8

Translation

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P98-19	FOR FURTHER ACTION SecNotificationofTransmittalofInternational Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/JP98/02610	International filing date (day/month/year) 12 June 1998 (12.06.98)	Priority date (day/month/year)
International Parent Classification (IPC) or national classification and IPC C08L 51/04, 77/12, 25/12, C08K 5/42		
Applicant NIPPON A & L INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 22 September 1999 (22.09.99)	Date of completion of this report 02 June 2000 (02.06.2000)
Name and mailing address of the IPEA/JP	Authorized officer
Facsimile No.	Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/JP98/02610

I. Basis of the report

1. With regard to the elements of the international application:*

- ☒ the international application as originally filed
- ☐ the description:
 pages _____, as originally filed
 pages _____, filed with the demand
 pages _____, filed with the letter of _____
- ☐ the claims:
 pages _____, as originally filed
 pages _____, as amended (together with any statement under Article 19
 pages _____, filed with the demand
 pages _____, filed with the letter of _____
- ☐ the drawings:
 pages _____, as originally filed
 pages _____, filed with the demand
 pages _____, filed with the letter of _____
- ☐ the sequence listing part of the description:
 pages _____, as originally filed
 pages _____, filed with the demand
 pages _____, filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheets/fig. _____

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rule 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under Item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/JP98/02610

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-8	YES
	Claims		NO
Inventive step (IS)	Claims	1-8	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-8	YES
	Claims		NO

2. Citations and explanations

The subject matter of claims 1-8 is neither disclosed in any of the documents cited in the ISR, nor is it considered that said subject matter could easily have been arrived at by a person skilled in the art based on the disclosures in said documents.



特許協力条約に基づいて公開された国際出願

(51) 国際特許分類6 C08L 51/04, 77/12, 25/12, C08K 5/42	A1	(11) 国際公開番号 WO99/64512 (43) 国際公開日 1999年12月16日(16.12.99)
(21) 国際出願番号 PCT/JP98/02610 (22) 国際出願日 1998年6月12日(12.06.98) (71) 出願人 (米国を除くすべての指定国について) 日本エイアンドエル株式会社 (NIPPON A&L INC.)[JP/JP] 〒541-8550 大阪府大阪市中央区北浜4丁目5番33号 Osaka, (JP) 本田技研工業株式会社 (HONDA GIKEN KOGYO KABUSHIKI KAISHA)[JP/JP] 〒107-8556 東京都港区南青山2丁目1番1号 Tokyo, (JP) (72) 発明者 ; および (75) 発明者 / 出願人 (米国についてののみ) 神山史朗(KAMIYAMA, Shiro)[JP/JP] 小浜克己(KOHAMA, Katsumi)[JP/JP] 〒350-1381 埼玉県狭山市新狭山1丁目10-1 ホンダエンジニアリング株式会社内 Saitama, (JP) 青木寛充(AOKI, Hiromichi)[JP/JP] 〒569-1046 大阪府高槻市塚原2丁目10-1 日本エイアンドエル株式会社内 Osaka, (JP) 阪野 元(SAKANO, Hajime)[JP/TH] バンコク 10110 スクンビット ソイ 22 199 Bangkok, (TH)		高川泰延(TAKAGAWA, Yasunobu)[JP/JP] 〒567-0021 大阪府茨木市三島丘2-24-21 丹羽マンション305 Osaka, (JP) (74) 代理人 弁理士 三枝英二, 外(SAEGUSA, Eiji et al.) 〒541-0045 大阪府大阪市中央区道修町1-7-1 北浜TNKビル Osaka, (JP) (81) 指定国 CA, US, 欧州特許 (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE) 添付公開書類 国際調査報告書
(54)Title: RESIN COMPOSITION FOR ELECTROSTATIC COATING (54)発明の名称 静電塗装用樹脂組成物 (57) Abstract A resin composition for electrostatic coating, characterized by comprising a rubber-reinforced aromatic vinyl resin (A), a polyamide elastomer (B), a modified vinyl polymer (C) containing at least one functional group selected from among carboxyl, epoxy, amino and amido, and an alkali metal salt (D); articles molded from the resin composition and excellent in electrostatic coatability; and products produced by coating the articles electrostatically.		

本発明は、（Ａ）ゴム強化芳香族ビニル樹脂、（Ｂ）ポリアミドエラストマー、（Ｃ）カルボキシル基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも１種の官能基を含む変性ビニル重合体、並びに（Ｄ）アルカリ金属塩を含有することを特徴とする静電塗装用樹脂組成物、該樹脂組成物から形成される静電塗装性に優れた樹脂成形品、並びに該樹脂成形品に静電塗装を施してなる静電塗装成形品を提供する。

PCTに基づいて公開される国際出願のパンフレット第一頁に掲載されたPCT加盟国を同定するために使用されるコード(参考情報)

AE	アラブ首長国連邦	DM	ドミニカ	KZ	カザフスタン	RU	ロシア
AL	アルバニア	EE	エストニア	LC	セントルシア	SD	スーダン
AM	アルメニア	ES	スペイン	LI	リヒテンシュタイン	SE	スウェーデン
AT	オーストリア	FI	フィンランド	LK	スリランカ	SG	シンガポール
AU	オーストラリア	FR	フランス	LR	リベリア	SI	スロヴェニア
AZ	アゼルバイジャン	GA	ガボン	LS	レソト	SK	スロヴァキア
BA	ボスニア・ヘルツェゴビナ	GB	英国	LT	リトアニア	SL	シエラ・レオネ
BB	バルバドス	GD	グレナダ	LU	ルクセンブルグ	SN	セネガル
BE	ベルギー	GE	グルジア	LV	ラトヴィア	SZ	スワジランド
BF	ブルキナ・ファソ	GH	ガーナ	MA	モロッコ	TD	チャード
BG	ブルガリア	GM	ガンビア	MC	モナコ	TG	トーゴ
BJ	ベナン	GN	ギニア	MD	モルドヴァ	TJ	タジキスタン
BR	ブラジル	GW	ギニア・ビサウ	MG	マダガスカル	TZ	タンザニア
BY	ベラルーシ	GR	ギリシャ	MK	マケドニア旧ユーゴスラヴィア共和国	TM	トルクメニスタン
CA	カナダ	HR	クロアチア			TR	トルコ
CF	中央アフリカ	HU	ハンガリー	ML	マリ	TT	トリニダード・トバゴ
CG	コンゴ	ID	インドネシア	MN	モンゴル	UA	ウクライナ
CH	スイス	IE	アイルランド	MR	モリタニア	UG	ウガンダ
CI	コートジボアール	IL	イスラエル	MW	マラウイ	US	米国
CM	カメルーン	IN	インド	MX	メキシコ	UZ	ウズベキスタン
CN	中国	IS	アイスランド	NE	ニジェール	VN	ヴェトナム
CR	コスタ・リカ	IT	イタリア	NL	オランダ	YU	ユーゴスラビア
CU	キューバ	JP	日本	NO	ノルウェー	ZA	南アフリカ共和国
CY	キプロス	KE	ケニア	NZ	ニュージーランド	ZW	ジンバブエ
CZ	チェッコ	KG	キルギスタン	PL	ポーランド		
DE	ドイツ	KP	北朝鮮	PT	ポルトガル		
DK	デンマーク	KR	韓国	RO	ルーマニア		

明 細 書

静電塗装用樹脂組成物

技術分野

本発明は、静電塗装用樹脂組成物、該樹脂組成物から
5 形成される樹脂成形品、及び静電塗装された樹脂成形品
に関するものである。

背景技術

ゴム強化スチレン樹脂は、耐衝撃性、成形性等に優れた
ものであり、車両分野、電気製品、事務機器等の広範
10 な分野に利用されている。

中でも、車両分野への応用が多く、装飾及び耐候性改良
のために塗装が行なわれる場合が多い。

しかしながら、ゴム強化スチレン樹脂の成形品に塗装
を行った場合、塗料の塗着効率が悪く、また、複雑な形
15 状を有する成形品では、塗装表面の品質が均一に保てない
という問題がある。

これらの問題を解決するための塗装方法として静電塗装
が従来から行なわれている。しかしながら、この方法
では、本来ゴム強化スチレン系樹脂が絶縁材料であるため、
20 む、予め成形品表面に導電プライマー処理工程が必要である。
また、導電カーボンを樹脂に配合する方法もとられているが、
形成される塗膜の衝撃強度等の低下が大きい。

いという欠点がある。

発明の開示

本発明は、上記問題点を解決すべく成されたものであり、その主な目的は、ゴム強化スチレン樹脂の様なゴム強化芳香族ビニル樹脂を含有する樹脂組成物であって、
5 該樹脂組成物から形成される成形品は、耐衝撃性等の各種物性に優れ、しかも導電プライマー処理を行うことなく、良好な静電塗装皮膜を形成することができる静電塗装用樹脂組成物を提供することである。

10 本発明の他の目的は、ゴム強化芳香族ビニル樹脂を含有する樹脂組成物から得られた静電塗装性及び各種物性に優れた樹脂成形品を提供することである。

本発明者は、上述した如き従来技術に鑑みて鋭意研究を重ねた結果、特定のゴム強化芳香族ビニル樹脂、ポリ
15 アミドエラストマー、特定の官能基を含む変性ビニル重合体及びアルカリ金属塩を含む樹脂組成物により形成される樹脂成形品は、導電プライマーを施さない場合であっても、良好な静電塗装皮膜を形成することができ、しかも、該成形品は耐衝撃性等の各種の物性に優れたもの
20 となることを見出し、ここに本発明を完成するに至った。

即ち、本発明は、下記の樹脂組成物、樹脂成形品、及び静電塗装された樹脂成形品を提供するものである。

1. (A) ゴム強化芳香族ビニル樹脂、(B) ポリアミドエラストマー、(C) カルボキシル基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも1種の官能基を含む変性ビニル重合体、並びに(D) アルカリ金属塩を含有することを特徴とする静電塗装用樹脂組成物。
5
2. ゴム強化芳香族ビニル樹脂(A) が、ゴム状重合体(a-1)の存在下に、(i) 芳香族ビニル単量体、(ii) シアン化ビニル単量体及び不飽和カルボン酸アルキルエステル単量体から選ばれた少なくとも一種の単量体、
10 並びに(iii) 必要に応じて、共重合可能な他のビニル系単量体からなる単量体(a-2)を重合して得られるグラフト共重合体、又は単量体(a-2)の共重合体と該グラフト共重合体の混合物である上記項1に記載の樹脂組成物。
- 15 3. ポリアミドエラストマー(B) が、炭素数が6以上のアミノカルボン酸、炭素数が6以上のラクタム及び $m + n \geq 12$ のナイロン $m n$ 塩の少なくとも一種と、ポリオールとを反応させて得られるものである上記項1に記載の樹脂組成物。
- 20 4. 変性ビニル重合体(C) が、カルボキシル基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも1種の官能基を含むエチレン系不飽和単量体と他のエチ

レン系不飽和単量体との共重合体である上記項 1 に記載の樹脂組成物。

5 5. アルカリ金属塩 (D) が、ドデシルベンゼンスルホン酸のアルカリ金属塩およびチオシアン酸カリウムから選ばれた少なくとも一種である上記項 1 に記載の樹脂組成物。

6. (A) ゴム強化芳香族ビニル樹脂、(B) ポリアミドエラストマー、(C) 変性ビニル重合体、及び (D) アルカリ金属塩の合計量を 100 重量%として、ゴム強化芳香族ビニル樹脂 (A) 2 ~ 96.95 重量%、ポリアミドエラストマー (B) 2 ~ 96.95 重量%、変性ビニル重合体 (C) 1 ~ 50 重量%、及びアルカリ金属塩 (D) 0.05 ~ 10 重量%を含有する上記項 1 ~ 5 のいずれかに記載の樹脂組成物。

15 7. 上記項 1 ~ 6 のいずれかに記載の樹脂組成物を成形してなる静電塗装性に優れた樹脂成形品。

8. 上記項 7 に記載の樹脂成形品に静電塗装を施してなる静電塗装成形品。

20 本発明の静電塗装用樹脂組成物は、(A) ゴム強化芳香族ビニル樹脂、(B) ポリアミドエラストマー、(C) カルボキシ基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも一種の官能基を含む変性ビニル重

合体、並びに（D）アルカリ金属塩を含有するものである。

以下に、本発明の樹脂組成物に含まれる各成分について、説明する。

5 （A）ゴム強化芳香族ビニル樹脂

 ゴム強化芳香族ビニル樹脂とは、ゴム強化スチレン系樹脂とも称されるものであり、ゴム状重合体（a-1）と、（i）芳香族ビニル単量体、（ii）シアン化ビニル単量体及び不飽和カルボン酸アルキルエステル単量体から選ばれた少なくとも一種の単量体、並びに（iii）必要
10 に応じて、共重合可能な他のビニル系単量体からなる単量体（a-2）を重合してなる樹脂である。該ゴム強化芳香族ビニル樹脂は、好ましくは、（a-1）ゴム状重合体の存在下に、単量体（a-2）を重合してなるグラ
15 フト共重合体、又は単量体（a-2）を重合してなる共重合体と上記グラフト共重合体の混合物である。

 以下に、ゴム強化芳香族ビニル樹脂を構成する各成分について説明する。

 （a-1）ゴム状重合体

20 ゴム状重合体（a-1）としては、例えば、ポリブタジエン、スチレン-ブタジエン共重合体、アクリロニトリル-ブタジエン共重合体等のジエン重合体、エチレン

ープロピレン共重合体、エチレンープロピレンー非共役
ジエン共重合体等のエチレンープロピレン系共重合体、
アクリル酸エステル系共重合体、塩素化ポリエチレン等
が挙げられる。これらのゴム状重合体（a-1）は、一
5 種単独または二種以上混合して用いることができる。

ゴム状重合体の製造方法については、特に限定はなく、
公知の条件に従って、乳化重合、溶液重合、懸濁重合、
塊状重合等により製造することができる。ゴム状重合体
のゲル含有率については、特に限定的ではないが、0～
10 95%であることが望ましい。特に、ゴム状重合体は、
ゲル含有率の制御の容易さから、乳化重合法で製造する
ことが望ましい。

（a-2）単量体

単量体（a-2）は、（i）芳香族ビニル単量体、
15 （ii）シアン化ビニル単量体及び不飽和カルボン酸アル
キルエステル単量体から選ばれた少なくとも一種の単量
体、並びに（iii）必要に応じて、共重合可能な他のビニ
ル単量体からなるものである。

（i）芳香族ビニル単量体としては、例えば、スチレ
20 ン、 α -メチルスチレン、 o -メチルスチレン、 m -メ
チルスチレン、 p -メチルスチレン、 t -ブチルスチレ
ン、 α -メチルビニルトルエン、ジメチルスチレン、ク

ロルスチレン、ジクロルスチレン、ブロムスチレン、ジブロムスチレン、ビニルナフタレン等を用いることができ、特にスチレンが好ましい。芳香族ビニル単量体は、一種単独または二種以上混合して用いることができる。

- 5 (ii) シアン化ビニル単量体と不飽和カルボン酸アルキルエステル単量体は、いずれか一方又は両方を混合して用いることができる。

シアン化ビニル単量体としては、例えば、アクリロニトリル、メタクリロニトリル、フマロニトリル等を用い
10 ることができる、特にアクリロニトリルが好ましい。

不飽和カルボン酸アルキルエステル系単量体としては、例えば、メチル（メタ）アクリレート、エチル（メタ）アクリレート、プロピル（メタ）アクリレート、2-エチルヘキシル（メタ）アクリレート等を用いることができ、
15 メチルメタクリレートが特に好ましい。

これらの単量体は、一種単独又は二種以上混合して用いることができる。

本発明では、特に、単量体(ii)としては、シアン化ビニル単量体を用いることが好ましい。

- 20 (iii) 共重合可能な他のビニル単量体は、上述の(i)芳香族ビニル単量体、並びに(ii)シアン化ビニル単量体及び不飽和カルボン酸アルキルエステル単量体から選

ばれた少なくとも一種の単量体と共重合可能な単量体であれば良いが、好ましくは、ゴム状重合体との共重合性も有するビニル単量体が良い。

この様な単量体の具体例としては、アクリル酸、メタ
5 クリル酸、マレイン酸などの不飽和カルボン酸、マレイン酸無水物、シトラコン酸無水物などの不飽和ジカルボン酸無水物、マレイミド、メチルマレイミド、エチルマレイミド、N-フェニルマレイミド、O-クロル-N-フェニルマレイミドなどのマレイミド化合物等を挙げる
10 ことができる。共重合可能な他のビニル系単量体は一種単独又は二種以上混合して用いることができる。

(iv) 単量体 (a-2) の組成比率

単量体 (a-2) における、芳香族ビニル単量体 (単
量体 (i))、シアン化ビニル単量体および不飽和カル
15 ボン酸アルキルエステル単量体から選ばれた少なくとも一種の単量体 (単量体 (ii))、並びに共重合可能な他のビニル単量体 (単量体 (iii)) の使用割合については、特に制限はないが、単量体 (i)、(ii) 及び (iii) の
合計量を 100 重量%とした場合に、単量体 (i) 50
20 ~ 90 重量%、単量体 (ii) 50 ~ 10 重量%、および単量体 (iii) 0 ~ 40 重量%であることが好ましく、単量体 (i) 50 ~ 80 重量%、単量体 (ii) 50 ~ 20

重量%、および単量体 (iii) 0 ~ 30 重量%であることがより好ましい。

ゴム強化芳香族ビニル樹脂 (A) の製法

5 ゴム強化芳香族ビニル樹脂 (A) の製造方法については特に制限はないが、上述のゴム状重合体 (a-1) の存在下に、単量体 (a-2) を重合してグラフト共重合体を製造する方法が好ましい。この際の重合方法自体は、公知の乳化重合、懸濁重合、塊状重合、溶液重合またはこれらを組み合わせた方法が用いられる。

10 上記した方法によって得られるグラフト共重合体のグラフト率および重量平均粒子径については特に制限はないが、グラフト率 20 ~ 100 % 程度、および重量平均粒子径 0.05 ~ 5 μ m 程度であることが好ましい。

15 本発明で用いるゴム強化芳香族ビニル樹脂 (A) は、上記グラフト共重合体単独であっても良く、或いは、上記グラフト重合体と、単量体 (a-2) の共重合体を混合したものでも良い。

20 ゴム強化芳香族ビニル樹脂 (A) を構成する上記グラフト共重合体と、単量体 (a-2) の共重合体の割合は、両者の合計量を 100 重量%として、グラフト共重合体 100 ~ 10 重量%及び単量体 (a-2) の共重合体 0 ~ 90 重量%であることが好ましい。グラフト共重合体

の割合が10重量%未満では、最終組成物の耐衝撃性が劣るものとなるので好ましくない。

尚、上記グラフト共重合体の製造時には、単量体（a-2）の共重合体も副生するが、上記したグラフト共重合体の割合には、グラフト共重合体の製造時に副生する単量体（a-2）の共重合体も含めるものとし、ここでいう単量体（a-2）の共重合体の割合とは、該グラフト共重合体とは別個に製造する単量体（a-2）の共重合体の割合である。単量体（a-2）の重合方法については、特に制限はなく、公知の乳化重合、懸濁重合、塊状重合、溶液重合またはこれらを組み合わせた方法を採用できる。

ゴム強化芳香族ビニル樹脂（A）におけるゴム状重合体（a-1）と単量体（a-2）の組成比率については、特に限定的ではないが、ゴム状重合体（a-1）と単量体（a-2）の合計量を100重量%として、ゴム状重合体（a-1）5～80重量%と単量体（a-2）95～20重量%であることが好ましく、ゴム状重合体（a-1）5～60重量%と単量体（a-2）95～40重量%であることがより好ましい。この場合に、グラフト重合体単独の場合には、該グラフト重合体中の組成

比率であり、グラフト重合体と共重合体の混合物の場合には、混合物全体に占める組成比率である。

(B) ポリアミドエラストマー

ポリアミドエラストマー (B) は、ポリエーテルエステルアミドとも称されるものであり、ハードセグメントとしての炭素数が 6 以上のアミノカルボン酸、炭素数が 6 以上のラクタム、及び $m + n \geq 12$ のナイロン $m n$ 塩の少なくとも一種（以下「(X) 成分」ということがある）と、ソフトセグメントとしてのポリオール（以下「(Y) 成分」ということがある）とを反応させて得られるものを用いることができる。

(X) 成分の中で、炭素数が 6 以上のアミノカルボン酸については、炭素数の上限は、12 程度のものが好ましく、具体例としては、 ω -アミノカプロン酸、 ω -アミノエナトン酸、 ω -アミノカプリル酸、 ω -アミノベルゴン酸、 ω -アミノカプリン酸、11-アミノウンデカン酸、12-アミノドデカン酸などを例示できる。

炭素数が 6 以上のラクタムとしては、炭素数の上限は、12 程度のものが好ましく、具体例としては、カプロラクタム、ラウロラクタムなどを例示できる。

ナイロン $m n$ 塩 ($m + n \geq 12$) は、炭素数 6 以上、好ましくは炭素数 6 ~ 12 のジカルボン酸と、炭素数 6

以上、好ましくは炭素数 6 ~ 12 のジアミンとの当モルからなる塩であり、具体例としては、ナイロン 6・6 塩、ナイロン 6・10 塩、ナイロン 6・12 塩、ナイロン 11・6 塩、ナイロン 11・10 塩、ナイロン 11・12 塩、
5 ナイロン 12・6 塩、ナイロン 12・10 塩、ナイロン 12・12 塩などが挙げられる。

(Y) 成分のポリオールとしては、例えば、ポリ(アルキレンオキシド)グリコールを用いることができ、具体例としては、ポリエチレングリコール、ポリ(1, 2
10 および 1, 3 プロピレンオキシド)グリコール、ポリ(テトラメチレンオキシド)グリコール、ポリ(ヘキサメチレンオキシド)グリコール、エチレンオキシドとプロピレンオキシドのブロックまたはランダム共重合体、エチレンオキシドとテトラヒドロフランのブロックまたは
15 はランダム共重合体などが挙げられる。これらのポリオールの平均分子量は、500 ~ 3000 程度が適当である。

ポリアミドエラストマー(B)の製造方法については、特に制限はなく、従来公知の方法を採用できる。例えば、
20 (X) 成分とジカルボン酸とを反応させてポリアミドプレポリマーを形成させて、これに(Y)成分であるポリオールを加えて、高温減圧下で重合する方法、(X)成

分、（Ｙ）成分、及びジカルボン酸を同時に反応槽に仕込み、高温で加圧反応させることによりカルボン酸末端のポリアミドエラストマーを生成させ、その後、常圧又は減圧下で重合を進める方法等により得ることができる。

5 ここで使用されるジカルボン酸は、好ましくは、炭素数４～２０のものであり、例えばテレフタル酸、イソフタル酸、フタル酸、ナフタレンー２，６ージカルボン酸、ナフタレンー２，７ージカルボン酸、ジフェニルー４，４ージカルボン酸、ジフェノキシエタンジカルボン酸、
10 ３ースルホイソフタル酸ナトリウム等の芳香族ジカルボン酸、１，４ーシクロヘキサンジカルボン酸、１，２ーシクロヘキサンジカルボン酸、ジシクロヘキシルー４，４ージカルボン酸等の脂環族ジカルボン酸、琥珀酸、シュウ酸、アジピン酸、ジカルボン酸等が挙げられる。

15 （Ｘ）成分と（Ｙ）成分の割合は、（Ｘ）成分と（Ｙ）成分の合計量を基準として、（Ｘ）成分の比率を９５～１０重量％程度とし、好ましくは、９０～２０重量％程度とする。（Ｘ）成分の比率が９５重量％を越えると柔軟性に劣るものとなり、１０重量％未満であると耐薬品
20 性に劣る傾向がある。

 本発明で使用するポリアミドエラストマーとしては、重量平均分子量が５，０００～１００，０００程度のも

のが適当である。

本発明で使用し得るポリアミドエラストマーの具体例としては、例えば、特開昭 6 2 - 2 3 2 4 5 0、特開昭 6 3 - 3 3 4 5 6、特開昭 6 3 - 9 5 2 5 1、特開平 1
5 - 6 0 6 4 7、特開平 1 - 2 4 0 5 5 3、特開平 3 - 9 7 7 5 1、特開平 4 - 3 0 9 5 4 7、特開平 4 - 3 1 4 7 4 1、特開平 4 - 3 4 8 1 5 0、特開平 5 - 2 3 0 3 6 5、特開平 5 - 2 6 2 9 7 1、特開平 5 - 2 8 7 1 6 1、特開平 5 - 2 9 5 1 9 1、特開平 5 - 3 2 0 4 9 7、
10 特開平 6 - 3 1 3 0 7 9、特開平 7 - 1 0 9 8 9、特開平 7 - 1 4 5 3 6 8、特開平 7 - 1 8 8 4 7 5、特開平 7 - 1 8 8 4 7 6 などに記載されるものを挙げる事ができる。

(C) 変性ビニル重合体

15 本発明で用いる変性ビニル重合体 (C) は、1 種または 2 種以上のビニル単量体を重合して得られるビニル重合体を基本骨格として、該重合体分子中にカルボキシル基、エポキシ基、アミノ基及びアミド基から選ばれる少なくとも 1 種の官能基を含むものである。これらの官能
20 基は、分子中に少なくとも一個存在することが必要である。

このような変性ビニル重合体の具体例としては、①官

能基を有するエチレン系不飽和単量体を重合してなる重合体、②官能基を有するエチレン系不飽和単量体と、他のエチレン系不飽和単量体との共重合体、③エチレン系不飽和単量体を重合するに際し、官能基を有する重合開始剤および／または官能基を有する連鎖移動剤を使用することにより重合体分子鎖中に官能基を導入してなる重合体等が挙げられる。

本発明で用いる変性ビニル重合体の内で、上記重合体①又は②を製造する際に用いることができる官能基を有するエチレン系不飽和単量体の具体例を挙げると、次の通りである。

カルボキシ基を有するエチレン系不飽和単量体としては、アクリル酸、メタクリル酸、マレイン酸、無水マレイン酸、イタコン酸等を例示できる。エポキシ基を有するエチレン系不飽和単量体としては、アクリル酸グリシジル、メタクリル酸グリシジル、イタコン酸グリシジル等を例示できる。アミノ基を有するエチレン系不飽和単量体としては、アクリル酸アミノエチル、メタクリル酸エチルアミノプロピル、メタクリル酸フェニルアミノエチルなどの（メタ）アクリル酸のアミノアルキルエステル誘導体、N-アセチルビニルアミンなどのビニルアミン誘導体、メタアリルアミンなどのアリルアミン誘導

体、アミノスチレン等を例示できる。アミド基を有するエチレン系不飽和単量体としては、アクリルアミド、N-メチルメタクリルアミド等を例示できる。

また、上記重合体②を製造する際に用いることができる他のエチレン系不飽和単量体としては、スチレン、 α -メチルスチレン、ビニルトルエン等の芳香族ビニル単量体、アクリロニトリル、メタクリロニトリル等のシアニ化ビニル単量体、アクリル酸メチル、メタクリル酸メチル、アクリル酸エチル、メタクリル酸エチル等のエチレン系不飽和カルボン酸エステル単量体、マレイミド、N-フェニルマレイミド、N-シクロヘキシルマレイミド等のマレイミド単量体等が挙げられる。

また、上記重合体③を製造する際に用いることができる官能基を有する重合開始剤の例としては、 γ , γ' -アゾビス(γ -シアノバレイン酸)、過酸化サクシン酸等のカルボキシル基を有する開始剤、 α , α' -アゾビス(γ -アミノ- α , γ -ジバレロニトリル)、p-アミノベンゾイルパーオキサイド等のアミノ基を有する開始剤等が挙げられる。また官能基を有する連鎖移動剤の例としては、メルカプトプロピオン酸、4-メルカプト安息香酸、チオグリコール酸等のカルボキシル基を有する連鎖移動剤、メルカプトメチルアミン、N-(β -メ

ルカプトエチル) - N - メチルアミン、ビス - (4 - アミノフェニル) ジスルフィド、メルカプトアニリン等のアミノ基を有する連鎖移動剤等が挙げられる。

5 変性ビニル重合体 (C) を重合する際の重合方法については、懸濁重合、塊状重合、乳化重合、溶液重合等いずれの方法によっても良く、特に限定されない。

上記重合体 ① 又は ② を製造する際には、重合開始剤、連鎖移動剤等としては、公知のものを用いることができる。例えば、重合開始剤としては、過硫酸カリウム、過酸化水素、過酸化ベンゾイル、過酸化ラウロイル等の過酸化物、アゾビスイソブチロニトリル等のアゾ化合物、クメンハイドロパーオキシド等の有機ハイドロパーオキシドと鉄塩等との酸化 - 還元系開始剤が挙げられる。また連鎖移動剤としては、n - ドデシルメルカプタン、t - ド
10 デシルメルカプタン等のメルカプタン類、 α - メチルスチレンダイマー、ターピノレン等が挙げられる。

上記重合体 ② の製造において、官能基を有するエチレン系不飽和単量体と、他のエチレン系不飽和単量体との組成比については、使用する単量体の種類によって、適
20 宜設定できるが、好ましくは、官能基を有するエチレン系不飽和単量体と、他のエチレン系不飽和単量体の合計量を基準として、官能基を有するエチレン系不飽和単量

体 0. 0 1 ~ 9 9 重量 % 及び他のエチレン系不飽和単量
体 1 ~ 9 9. 9 9 重量 % 程度であり、より好ましくは、
官能基を有するエチレン系不飽和単量体 0. 0 5 ~ 8 0
重量 % 及び他のエチレン系不飽和単量体 2 0 ~ 9 9. 9
5 5 重量 % 程度であり、更に好ましくは、官能基を有する
エチレン系不飽和単量体 0. 1 5 ~ 5 0 重量 % 及び他の
エチレン系不飽和単量体 5 0 ~ 9 9. 9 重量 % 程度であ
る。

また、上記製造方法③では、エチレン系不飽和単量体
10 の重合時に使用する官能基を有する重合開始剤と官能基
を有する連鎖移動剤の使用量については、特に限定的で
はないが、通常、エチレン系不飽和単量体 1 0 0 重量部
に対して、官能基を有する重合開始剤を 0. 0 1 ~ 5 重
量程度使用し、官能基を有する連鎖移動剤を 0. 0 1 ~
15 1 0 重量部程度使用すれば良い。官能基を有する重合開
始剤と官能基を有する連鎖移動剤は、両方を同時に用い
ても良く、或いは、一方だけが官能基を有するものであ
って、他方は、官能基を有しないものでも良い。製造方
法③では、エチレン系不飽和単量体としては、官能基を
20 有しないものを用いればよいが、勿論、官能基を有する
エチレン系不飽和単量体を用いても良い。

本発明では、特に、重合体中に占める官能基含有量の

制御の容易さ、最終組成物の物性バランスの面より、重合体②が好ましい。

(D) アルカリ金属塩

アルカリ金属塩 (D) としては、塩化リチウム、臭化
5 リチウム、ヨウ化リチウム、ヨウ化ナトリウム、ホウ水
素化ナトリウム、ホウフッ化リチウム、ホウフッ化カリ
ウム、テトラフェニルホウ酸リチウム、テトラフェニル
ホウ酸カリウム、テトラフェニルホウ酸ナトリウム、チ
オシアン酸リチウム、チオシアン酸ナトリウム、チオシ
10 アン酸カリウム、過塩素酸リチウム、過塩素酸ナトリウ
ム、過塩素酸カリウム等の無機酸のアルカリ金属塩；ト
リフルオロ酢酸リチウム、トリフルオロ酢酸ナトリウム、
トリフルオロ酢酸カリウム、トリフルオロメタンスルホ
ン酸リチウム、トリフルオロメタンスルホン酸ナトリウ
15 ム、トリフルオロメタンスルホン酸カリウム、酢酸リチ
ウム、酢酸ナトリウム、酢酸カリウム、ドデシルベンゼ
ンスルホン酸リチウム、ドデシルベンゼンスルホン酸カ
リウム、ドデシルベンゼンスルホン酸ナトリウム、ドデ
シルスルホン酸リチウム、ドデシルスルホン酸カリウム、
20 ドデシルスルホン酸ナトリウム等の有機酸のアルカリ金
属塩等を用いることができる。これらの金属塩は、一種
単独または二種以上を混合して用いることができる。

これらアルカリ金属塩の中で好ましいものは、ドデシルベンゼンスルホン酸の様な核置換ベンゼンスルホン酸のアルカリ金属塩およびチオシアン酸カリウムである。

本発明樹脂組成物及び樹脂成形体

5 本発明の樹脂組成物は、上記した（Ａ）ゴム強化芳香族ビニル樹脂、（Ｂ）ポリアミドエラストマー、（Ｃ）カルボキシル基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも一種の官能基を有する変性ビニル重合体、並びに（Ｄ）アルカリ金属塩を含有するものである。
10

 本発明の樹脂組成物は、上記した４成分を含めばよく、その形態については特に限定はなく、例えば、これらの各成分を粉末状等の状態で混合したものでもよいが、通常は、これらの各成分を混合し、熔融して、ペレット状態の組成物とし、その後成形品の製造に用いられる。
15

 各成分の混合方法、混合順序については、特に制限はなく、各成分の一括同時混合、或いは、２成分若しくは３成分を混合した後、残りの成分を混合してなる２段階以上の多段混合などを採用することが可能である。混合
20 に際しては、公知の混合装置、例えば、ニーダー、バンバリーミキサー、ロール等を用いることができる。その後、通常のペレタイザー等を用いてペレット化すること

によって、ペレット状態の組成物とすることができる。

本発明の樹脂組成物における各成分の割合は、特に限定的ではないが、(A)～(D)の4成分の合計量を100重量%として、ゴム強化芳香族ビニル樹脂(A)2
5 ～96.95重量%程度、ポリアミドエラストマー(B)2～96.95重量%程度、変性ビニル重合体(C)1～50重量%程度、及びアルカリ金属塩(D)0.05～10重量%程度とすることが好ましい。(A)～(D)の成分をこの様な配合割合で用いることによって、特に、
10 得られる樹脂組成物は流動性等が良好で成形作業性に優れたものとなり、該樹脂組成物から形成される成形品は、導電プライマーを施さない場合にも、良好な静電塗装皮膜を形成することが可能となる。しかも、この成形品は、耐衝撃性、機械的強度等の各種物性に優れ、寸法安定性、
15 外観等も良好になる。

上記各成分の中で、ゴム強化芳香族ビニル樹脂(A)が少なすぎる場合には、最終組成物の耐衝撃性、機械的強度が十分ではなく、また、流動性、外観、寸法安定性が悪くなる。一方、多すぎると塗料塗着効率が改善され
20 ない。

ポリアミドエラストマー(B)については、これが少ないと最終組成物の塗料塗着効率が改善されず、多くな

りすぎると剛性が低下する。

変性ビニル重合体（C）については、これが少なすぎると耐水性および塗装膜密着性に劣るものとなり、多すぎると機械的強度、流動性、成形品の外観に劣るものとなるので好ましくない。

アルカリ金属塩（D）については、少なすぎると塗料塗着効率に劣るものとなり、多すぎると熱安定性および成形品外観に劣るものとなるので好ましくない。

本発明では、特に、塗料塗着効率が良く、しかも剛性を含めた機械的特性が良好である点で、（A）～（D）の4成分の合計量を100重量%として、ゴム強化芳香族ビニル樹脂（A）50～90重量%程度、ポリアミドエラストマー（B）5～50重量%程度、変性ビニル重合体（C）3～20重量%程度、及びアルカリ金属塩（D）0.2～5重量%程度とすることがより好ましい。

本発明の樹脂組成物には、更に、必要に応じて、酸化防止剤〔例えば2, 6-ジ-tert-ブチル-4-メチルフェノール、2-（1-メチルシクロヘキシル）-4, 6-ジメチルフェノール、2, 2-メチレンビス-（4-エチル-6-tert-メチルフェノール）、4, 4'-チオビス-（6-tert-ブチル-3-メチルフェノール）、ジラウリルチオジプロピオネート、トリス（ジ-ノニル

フェニル) ホスファイト、ワックス〕、紫外線吸収剤
〔例えば p - t - ブチルフェニルサリシレート、2, 2
'- ジヒドロキシ - 4 - メトキシベンゾフェノン、2 -
(2' - ヒドロキシ - 4' - n - オクトキシフェニル)
5 ベンゾトリアゾール〕、滑剤〔例えばパラフィンワック
ス、ステアリン酸、硬化油、ステアロアミド、メチレン
ビスステアロアミド、エチレンビスステアロアミド、n
- ブチルステアレート、ケトンワックス、オクチルアル
コール、ラウリルアルコール、ヒドロキシステアリン酸
10 トリグリセリド〕、難燃剤〔例えば、酸化アンチモン、
水酸化アルミニウム、ほう酸亜鉛、トリクレジルホスフ
ェート、トリス(ジクロロプロピル)ホスフェート、塩
素化パラフィン、テトラブロモブタン、ヘキサブロモベ
ンゼン、テトラブロモビスフェノール A〕、着色剤〔例
15 えば酸化チタン、カーボンプラック〕、充填剤〔例えば
炭酸カルシウム、クレー、シリカ、ガラス繊維、ガラス
球、カーボン繊維〕、顔料等を添加することができる。

これらの添加剤は、それぞれの目的に応じて適宜添加
量を設定することができ、特に添加量が限定されるもの
20 ではないが、通常、(A) ~ (D) の成分の合計量 10
0 重量部に対して、添加剤成分の合計量が 0. 01 ~ 1
00 重量部程度、好ましくは、0. 01 ~ 50 重量部程

度の範囲となるようにすれば良い。

本発明の樹脂組成物には、更に、必要に応じて、ポリカーボネート、ポリ塩化ビニル、ポリアミド、ポリブチレンテレフタレート、ポリエチレンテレフタレート、ポリフェニレンオキサイド、ポリオキシメチレン等の他の熱可塑性樹脂を混合することができる。

これらの熱可塑性樹脂についても、それぞれの目的に応じて適宜添加量を設定することができ、特に添加量が限定されるものではないが、通常、(A)～(D)の成分の合計量100重量部に対して、熱可塑性樹脂の合計量が1～100重量部程度、好ましくは、1～50重量部程度の範囲となるようにすれば良い。

本発明の樹脂組成物を用いて目的とする成形品を得るには、目的とする成形品の種類に応じて、常法に従って、成形すれば良い。例えば、上記したペレット状態とした樹脂組成物を用いて、熔融樹脂温度200～280℃程度、金型温度30～100℃程度で、適宜、射出成形、押出成形、圧縮成形、ブロー成形等の公知の成形方法を採用して、目的とする成形品とすればよい。

本発明の樹脂組成物を用いて形成される成形品は、静電塗装性が良好であり、これに静電塗装を行う場合には、導電プライマー処理を施すことなく、常法に従って静電

塗装を行えば良い。形成される塗膜は、複雑な形状の成形品においても塗装表面の品質が均一となり、しかも、良好な密着性を有するものとなる。

発明の効果

- 5 本発明の樹脂組成物は、流動性等が良好で成形作業性が良く、該樹脂組成物から形成される成形品は、導電プライマーを施さない場合にも、良好な静電塗装皮膜を形成することができる。しかも、この成形品は耐衝撃性、機械的強度等の各種物性に優れ、寸法安定性、外観等も
- 10 良好である。

この様な樹脂成形品は、車両用部品、電気製品、事務機器等の広範な分野に利用し得るものであり、特に、車両用部品等として好適に使用できる。

発明を実施するための最良の形態

- 15 次に本発明を実施例に基づいて説明するが、本発明はかかる実施例のみに限定されるものではない。なお、配合組成における部および％は全て重量に基づくものである。

〔実施例 1 ～ 3、比較例 1 ～ 5〕

- 20 実施例及び比較例で用いた成分は以下のものである。

・ゴム強化芳香族ビニル樹脂（A）

A - 1 : ポリブタジエンラテックス（平均粒子径 0. 3

5 $5\ \mu\text{m}$ 、ゲル含有量 80%) 20 部 (固形分)、スチレン 55 部およびアクリロニトリル 25 部を公知の乳化重合法により重合した。得られた重合体ラテックスを塩析、脱水、乾燥処理し、A-1 を得た。

5 ・ポリアミドエラストマー (B)

B-1 : ポリエーテルエステルアミド (三洋化成社製、ペレスタット IOS-6321)

B-2 : ポリエーテルエステルアミド (東レ社製、ベパックス 4011MA)

10 ・変性ビニル重合体 (C)

C-1 : スチレン 70 部、アクリロニトリル 27 部およびアクリル酸 3 部を公知の乳化重合法により重合した。得られた重合体ラテックスを塩析、脱水、乾燥処理し、C-1 を得た。

15 ・アルカリ金属塩 (D)

D-1 : ドデシルベンゼンスルホン酸ナトリウム

上記各成分を表 1 に示す組成となるように配合して混合し、1 軸押出機にて 220 °C で熔融混練して、ペレットを得た。得られたペレットを用いて、下記の各方法により、各種物性を測定した。測定方法は、以下の通りである。測定結果を表 1 に示す。

耐衝撃性（ノッチ付アイゾット）

A S T M D - 2 5 6 に準拠した方法により、成形温度 2 3 0 °C で 1 / 4 インチ厚の試験片を成形し、2 3 °C でノッチ付アイゾット衝撃強度を測定した。

5 流動性

A S T M D - 1 2 3 8 に準拠した方法により、熔融温度 2 4 0 °C、荷重 1 0 k g の条件で流動性を測定した。

剛性

10 A S T M D - 7 9 0 に準拠した方法により、成形温度 2 3 0 °C で 1 / 4 インチ厚の試験片を成形し、2 3 °C で曲げ弾性率を測定した。

成形収縮率

15 彫り込み寸法 1 5 0 m m × 9 0 m m × 3 m m 厚の金型を用い、成形温度 2 3 0 °C で射出成形し、成形品を得た。成形後、室温で 7 2 時間放置した後、成形品の寸法をノギスを使用して 0 . 0 1 m m まで測定し、次式にて算出した。

$$\text{成形収縮率（％）} = \frac{\text{金型寸法} - \text{成形品寸法}}{\text{金型寸法}} \times 100$$

20

表面固有抵抗値

彫り込み寸法 1 5 0 m m × 9 0 m m × 3 m m 厚の金型

を用い、成形温度 230℃で射出成形し、成形品を得た。
試験片を 23℃、55%相対湿度の条件で 24 時間状態
調節した後、表面高抵抗計 SM-10E（東亜電波工業
（株）製）を用い、測定電圧 500 V、サンプリング時
5 間 10 秒の条件にて表面固有抵抗値を測定した。

成形品外観

彫り込み寸法 90 mm × 55 mm × 3 mm 厚の金型を
用い、成形温度 230℃で射出成形し、成形品を得た。
得られた成形品の艶ムラの状態を目視により観察し、下
10 記の基準で評価した。

A：良好 ～ C：不良

塗料塗着重量および密着性

彫り込み寸法 240 mm × 250 mm × 3.5 mm 厚
の金型を用い、成形温度 230℃で射出成形し、成形品
15 を得た。得られた成形品につき、下記条件にて静電塗装
を行った。

塗装機：レシプロ型回転式静電塗装機（ホンダエン
지니어リング製 IVW ベル型塗装機）

ベル直径 70 φ

20 印可電圧 - 60 K v

吐出量 100 g / min

ガン距離 200 mm

回転数 1 0 0 0 0 r p m

シェービングエアー 0. 4 k g

C V スピード 5 4 0 0 m m / m i n

レシプロスピード 2 6 0 0 m m / m i n

5 塗料 : 2 液硬化ウレタン塗料 (日本油脂製 ハイ
ウレタン # 5 0 0 0 、 # 6 5 0 0)

塗装条件 : 温度 2 7 ° C 、 湿度 6 5 % R H

上記条件で静電塗装を行った後、8 0 ° C で 2 時間乾燥
10 させて、塗料塗着重量を測定した。

また、上記静電塗装された成形品の塗膜の密着性を以下の方法にて測定した。

すなわち、片刃カミソリの切刃を塗面に対して約 3 0
度に保持し、素地に達する 1 m m の碁盤目 1 0 0 個 (1
15 0 × 1 0) を作成し、2 4 m m 幅のセロハン粘着テープ
を碁盤目上に完全に密着させ、直ちにテープの一端を有効面に直角に保ち瞬間的に引き離し、塗膜密着性を調べた。結果は、塗膜の剥離した個数 / テスト数 (1 0 0)
にて表す。

20 なお、塗装後の環境条件を変更し、次の 2 つの測定を行った。

条件 1 ; 湿度 9 5 % 、 5 0 ° C × 1 2 0 時間放置後の密

着 性

条 件 2 ; 湿 度 9 5 %、 5 0 °C × 2 4 0 時 間 放 置 後 の 密
着 性

5

10

15

20

表 1

	実 施 例			比 較 例				
	1	2	3	1	2	3	4	5
一 組成 - (部)								
A-1	70	50	85	100	80	40	70	25
B-1	18	18	8	-	20	58	20	18
B-2	-	15	-	-	-	-	-	-
C-1	10	15	5	-	-	-	10	55
D-1	2	2	2	-	-	2	-	2
一 物性 -								
耐衝撃性 (kg・cm/cm)	28	32	22	20	23	42	27	12
流動性 (g/10 min)	36	61	28	25	43	68	35	17
剛性 (kg/cm ²)	1.8×10^{-4}	1.4×10^{-4}	1.8×10^{-4}	2.4×10^{-4}	1.7×10^{-4}	0.9×10^{-4}	1.8×10^{-4}	2.1×10^{-4}
成形収縮率 (%)	0.6	0.9	0.6	0.5	0.6	1.1	0.7	0.6
表面固有抵抗 (Ω)	2.0×10^9	7.0×10^8	1.0×10^{10}	$>10^{16}$	3.0×10^{12}	7.0×10^7	3.5×10^{11}	5.2×10^9
成形品外觀	A	A	A	A	A	A	A	C
塗料塗着重量 (g)	1.02	1.09	0.85	0.17	0.55	1.12	0.52	0.82
密着性 条件1	100/100	100/100	100/100	100/100	3/100	0/100	100/100	100/100
密着性 条件2	100/100	100/100	100/100	100/100	0/100	0/100	100/100	100/100

請 求 の 範 囲

1. (A) ゴム強化芳香族ビニル樹脂、(B) ポリアミドエラストマー、(C) カルボキシル基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも1種の官能基を含む変性ビニル重合体、並びに(D) アルカリ金属塩を含有することを特徴とする静電塗装用樹脂組成物。
2. ゴム強化芳香族ビニル樹脂(A)が、ゴム状重合体(a-1)の存在下に、(i) 芳香族ビニル単量体、(ii) シアン化ビニル単量体及び不飽和カルボン酸アルキルエステル単量体から選ばれた少なくとも一種の単量体、並びに(iii) 必要に応じて、共重合可能な他のビニル系単量体からなる単量体(a-2)を重合して得られるグラフト共重合体、又は単量体(a-2)の共重合体と該グラフト共重合体の混合物である請求項1に記載の樹脂組成物。
3. ポリアミドエラストマー(B)が、炭素数が6以上のアミノカルボン酸、炭素数が6以上のラクタム及び $m + n \geq 12$ のナイロン $m n$ 塩の少なくとも一種と、ポリオールとを反応させて得られるものである請求項1に記載の樹脂組成物。

4. 変性ビニル重合体（C）が、カルボキシ基、エポキシ基、アミノ基及びアミド基から選ばれた少なくとも1種の官能基を含むエチレン系不飽和単量体と他のエチレン系不飽和単量体との共重合体である請求項1に記載の樹脂組成物。

5. アルカリ金属塩（D）が、ドデシルベンゼンスルホン酸のアルカリ金属塩およびチオシアン酸カリウムから選ばれた少なくとも一種である請求項1に記載の樹脂組成物。

6. （A）ゴム強化芳香族ビニル樹脂、（B）ポリアミドエラストマー、（C）変性ビニル重合体、及び（D）アルカリ金属塩の合計量を100重量%として、ゴム強化芳香族ビニル樹脂（A）2～96.95重量%、ポリアミドエラストマー（B）2～96.95重量%、変性ビニル重合体（C）1～50重量%、及びアルカリ金属塩（D）0.05～10重量%を含有する請求項1～5のいずれかに記載の樹脂組成物。

7. 請求項1～6のいずれかに記載の樹脂組成物を成形

してなる静電塗装性に優れた樹脂成形品。

8. 請求項7に記載の樹脂成形品に静電塗装を施してなる静電塗装成形品。

5

10

15

20

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 361 712
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89309082.9

(22) Date of filing: 07.09.89

(51) Int. Cl.⁵: **C08L 77/00 , C08L 77/12 ,
C08L 51/06 , C08L 55/02 ,
C08L 75/04 , C08L 25/08 ,
C08L 25/10**

(30) Priority: 07.09.88 JP 222392/88
16.09.88 JP 229751/88

(43) Date of publication of application:
04.04.90 Bulletin 90/14

(84) Designated Contracting States:
DE GB NL

(71) Applicant: **JAPAN SYNTHETIC RUBBER CO.,
LTD.**
11-24, Tsukiji-2-chome Chuo-ku
Tokyo 104(JP)

(72) Inventor: **Uehara, Shotaro**
Aobaryo, 29, Aobadai-2-chome
Midori-ku Yokohama(JP)
Inventor: **Mizuno, Hodaka**
1, Morigayamacho
Yokkaichi-shi(JP)
Inventor: **Atomori, Seiichi**
664-4 Koike
Nishibessho Kuwana-shi(JP)
Inventor: **Furuyama, Tateki**
1 Morigayamacho
Yokkaichi-shi(JP)
Inventor: **Kamiya, Akira**
5-436, Sakuradai-2-chome
Yokkaichi-shi(JP)

(74) Representative: **Clifford, Frederick Alan et al**
MARKS & CLERK 57/60 Lincoln's Inn Fields
London WC2A 3LS(GB)

(54) Thermoplastic resin composition.

EP 0 361 712 A1

(57) A thermoplastic resin composition comprising

(A) 1-90% by weight of a polyamide elastomer and

(B) 99-10% by weight of at least one of the following (a) and (b):

(a) a rubber-modified thermoplastic styrene resin consisting of a rubber-modified styrene polymer containing a hydroxyl group-containing alkenyl monomer as a copolymerized component or a mixture of rubber-modified styrene polymer with a styrene polymer, in which mixture at least one of these polymers contains a hydroxyl group-containing alkenyl monomer as a copolymerized component,

(b) a mixture or reaction product of (1) 40-99% by weight of a thermoplastic polyurethane with (2) 60-1% by weight of a functional group-containing styrene resin in which a styrene resin is copolymerized with an unsaturated compound having at least one functional group selected from the group consisting of a carboxyl group, an acid anhydride group, an amino group, an epoxy group and a hydroxyl group.

THERMOPLASTIC RESIN COMPOSITION

This invention relates to a thermoplastic resin composition superior in mechanical properties, moldability, permanent antistatic property, heat resistance during molding and surface appearance.

Synthetic polymer materials are in use in extensive fields because of their excellent properties; however, generally, they have a high electric resistivity and are easily electrified, and hence, various inconveniences are caused by static electricity. In order to endow synthetic polymer materials with an antistatic property, it has generally been conducted to (1) knead into a synthetic polymer a water-absorbent compound (e.g. polyalkylene oxide), an antistatic agent or the like, or (2) coat the surface of a synthetic polymer with a surfactant or the like. However, no sufficient antistatic property has been imparted by any of these methods. That is, the antistatic property of the synthetic polymer thus treated is lost by water-washing or surface-wiping or the compound incorporated is bled out by water-washing or surface-wiping, resulting in quality deterioration, whereby the quality of the synthetic polymer is deteriorated and the anti-static property thereof is deteriorated with the lapse of time.

Meanwhile, it is known that so-called polyetheresteramides in which a polyamide and a polyester are ester-bonded via a dicarboxylic acid have an excellent rubber elasticity and a good antistatic property. However, the polyetheresteramides have a rubber elasticity and insufficient mechanical strengths, and consequently, are not satisfactory as structural materials in which rigidity and high toughness are required. Moreover, the polyetheresteramides have poor compatibility with other thermoplastic resins, for example, vinyl polymers such as polystyrene, styrene-acrylonitrile copolymer (AS resin), polymethyl methacrylate, styrene-methyl methacrylate copolymer, acrylonitrile-butadiene-styrene terpolymer (ABS resin) and the like. Hence, for example, Japanese Patent Application Kokai No. 61-246244 (hereinafter referred to as "Prior Art 1") discloses that a composition consisting of (I) a polyetheresteramide, (II) a graft copolymer obtained by graft polymerizing a (meth)acrylic acid ester and/or an aromatic vinyl compound onto a rubbery polymer and (III) a copolymer (a styrene polymer) obtained by copolymerizing a mixture of a (meth)acrylic acid ester and an aromatic vinyl compound and/or a vinyl cyanide has a permanent antistatic property.

The composition of Prior Art 1, however, is not satisfactory in mechanical strengths such as impact strength and the like because the compatibility between the polyetheresteramide and the styrene copolymer is still poor, and accordingly the composition cannot be used in practice.

Japanese Patent Application Kokai No. 60-23435 (hereinafter referred to as "Prior Art 2") discloses blending a polyetheresteramide with a carboxyl group-containing modified vinyl polymer. However, the composition of Prior Art 2 have improved mechanical strength but exhibits poor appearance in respect of silver streaks, delustering and the like. Moreover, the composition of Prior Art 2, when allowed to reside during molding, not only is the above-mentioned poor appearance exhibited, but also the mechanical strength is lowered and the heat stability becomes inferior.

An object of this invention is to solve the above-mentioned problems of the prior art and provide a thermoplastic resin composition superior in heat stability during molding, moldability and permanent antistatic property.

According to this invention, there is provided a thermoplastic resin composition comprising (A) 1-90% by weight of a polyamide elastomer and (B) 99-10% by weight of at least one of the following (a) and (b):

(a) a rubber-modified thermoplastic styrene resin consisting of a rubber-modified styrene polymer containing a hydroxyl group-containing alkenyl monomer as a copolymerized component or a mixture of a rubber-modified styrene polymer and a styrene polymer, in which mixture at least one of these polymers contains a hydroxyl group-containing alkenyl monomer as a copolymerized component,

(b) a mixture or reaction product of (1) 40-99% by weight of a thermoplastic polyurethane and (2) 60-1% by weight of a functional group-containing styrene resin in which a styrene resin is copolymerized with an unsaturated compound having at least one functional group selected from the group consisting of a carboxyl group, an acid anhydride group, an amino group, an epoxy group and a hydroxyl group.

An example of the polyamide elastomer (A) used in this invention is an elastomer composed of a hard segment (X) which is an aminocarboxylic acid or lactam having 6 or more carbon atoms or a nylon mn salt in which $m + n$ is 12 or more and a soft segment (Y) which is a polyol, specifically a poly(alkylene oxide)-glycol, in which elastomer the proportion of the (X) component is 10-95% by weight, preferably 20-90% by weight, more preferably 80-90% by weight.

When the proportion of the (X) segment in the polyamide elastomer (A) is less than 10% by weight, the polyamide elastomer has poor compatibility with the component (B). When the proportion is more than 95% by weight, the polyamide elastomer is inferior in antistatic property.

The (X) segment, i.e. the aminocarboxylic acid or lactam having 6 or more carbon atoms and the nylon

mn salt in which $m + n$ is 12 or more include aminocarboxylic acids such as ω -aminocaproic acid, ω -aminoenanthic acid, ω -aminocaprylic acid, ω -aminopelargonic acid, ω -aminocapric acid, 11-aminoundecanoic acid, 12-aminododecanoic acid and the like; lactams such as caprolactam, lauro lactam and the like; and nylon salts such as nylon 6,6, nylon 6,10, nylon 6,12, nylon 11,6, nylon 11,10, nylon 12,6 nylon 11,12, nylon 12,10, nylon 12,12 and the like.

The (Y) segment, i.e. the poly(alkylene oxide)glycol includes poly(ethylene oxide)glycol, poly(1,2-or 1,3-propylene oxide)glycol, poly(tetramethylene oxide)glycol, poly(hexamethylene oxide)glycol, an ethylene oxide-propylene oxide block or random copolymer, an ethylene oxide-tetrahydrofuran block or random copolymer, etc. Of these poly(alkylene oxide)glycols (Y), poly(ethylene oxide)glycol is particularly preferable because of its excellent antistatic property.

The number-average molecular weight of the poly(alkylene oxide)glycol (Y) is preferably 200-6,000, more preferably 250-4,000.

In this invention, the terminals of the poly(alkylene oxide)glycol (Y) may be aminated or carboxylated.

As the bond between the (X) component and the (Y) component, an ester bond or an amide bond is possible depending upon the terminal groups of the polyamide elastomer (A).

In bonding the (X) component to the (Y) component, a third component (Z) such as a dicarboxylic acid, a diamine or the like can be used.

The dicarboxylic acid is such as to have 4-20 carbon atoms and includes, for example, aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-2,7-dicarboxylic acid, diphenyl-4,4-dicarboxylic acid, diphenoxyethanedicarboxylic acid, sodium 3-sulfoisophthalate and the like; alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid, 1,2-cyclohexanedicarboxylic acid, dicyclohexyl-4,4-dicarboxylic acid and the like; aliphatic dicarboxylic acids such as succinic acid, oxalic acid, adipic acid, sebacic acid, dodecanedicarboxylic acid and the like; and their mixtures. Of these, terephthalic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, sebacic acid, adipic acid and dodecanedicarboxylic acid are particularly preferable in view of polymerizability, color and physical properties.

The diamine includes aromatic, alicyclic and aliphatic diamines. An example of the aliphatic diamines is hexamethylenediamine.

The method of the synthesis of the polyamide elastomer (A) is not critical and may be, for example, the method disclosed in Japanese Patent Application Kokoku No. 56-45419, Japanese Patent Application Kokai No. 55-133424 or the like.

When there is used, as the polyamide elastomer (A), a polyetheresteramide composed of (X') an aminocarboxylic acid or lactam having 6 or more carbon atoms or a nylon mn salt in which $m + n$ is 12 or more, (Y') a poly(ethylene oxide)glycol having a number-average molecular weight of 200-6,000 and (Z') a dicarboxylic acid having 4-20 carbon atoms, in which polyetheresteramide the polyetherester unit is contained in an amount of 10-95% by weight, the resulting thermoplastic resin composition has a very high antistatic property.

The (X') component is preferably caprolactam, 12-aminododecanoic acid or nylon 6,6.

The (Y') component is preferably a poly(ethylene oxide)glycol having a number-average molecular weight of 250-4,000. When there is used a poly(ethylene oxide)glycol having a number-average molecular weight falling within the above range, the resulting thermoplastic resin composition is superior in mechanical properties and antistatic property.

The (Z') component is preferably terephthalic acid, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, sebacic acid, adipic acid or dodecanoic acid. When one of these dicarboxylic acids is used, the resulting polyamide elastomer is superior in polymerizability and color.

The rubber-modified thermoplastic styrene resin (B)(a) used in the composition of this invention is (a-1) a rubber-modified styrene polymer containing a hydroxyl group-containing alkenyl monomer as a copolymerized component or (a-2) a mixture of a rubber-modified styrene polymer and a rubber-unmodified styrene polymer, at least one of which contains a hydroxyl group-containing alkenyl monomer as a copolymerized component. This mixture is obtained by mixing a rubbery polymer with a specific styrene polymer in order to obtain a high impact resistance. The mixing may be effected by simple mechanical blending. In order to assure good compatibility, however, a so-called graft copolymerization is more preferable in which the styrene monomer is copolymerized in the presence of the rubbery polymer. It is also preferable to use a mixture obtained by a so-called graft-blending method in which a rubber-modified styrene polymer (graft copolymer) obtained by the above graft copolymerization is blended with a styrene polymer obtained by a separate method.

The rubbery polymer includes diene rubbers (e.g. polybutadiene, styrene-butadiene copolymer), acrylic copolymers, ethylene-propylene-(diene) copolymers, chlorinated polyethylene, polyurethane, etc.. Of these,

polybutadiene is preferable.

The rubber-modified thermoplastic styrene resin (B)(a) used in the composition of this invention contains a hydroxyl group-containing alkenyl monomer as a copolymerized component. In the case of (a-1), the rubber-modified styrene polymer contains a hydroxyl group-containing alkenyl monomer in the copolymerized form. In the case of (a-2), namely the mixture, at least one of the rubber-modified styrene polymer and the styrene polymer contains a hydroxyl group-containing alkenyl monomer in the copolymerized forms.

The styrene monomer constituting the styrene polymer includes styrene, α -methylstyrene, bromostyrene, etc. Of these, styrene is most preferable.

The hydroxyl group-containing alkenyl monomer is a compound having at least one unsaturation (double bond or triple bond) and at least one hydroxyl group. Typical examples of such a compound are alcohols having a double bond, alcohols having a triple bond, esters of an unsaturated mono- or di-carboxylic acid with an unsubstituted dihydric alcohol, esters of an unsaturated mono- or di-carboxylic acid with an unsubstituted trihydric alcohol, esters of an unsaturated mono- or di-carboxylic acid with an unsubstituted tetrahydric alcohol and esters of an unsaturated mono- or di-carboxylic acid with an unsubstituted pentahydric or more hydric alcohol.

Preferable examples of the hydroxyl group-containing alkenyl monomer used in this invention are 3-hydroxy-1-propane, 4-hydroxy-1-butene, cis-4-hydroxy-2-butene, trans-4-hydroxy-2-butene, 3-hydroxy-2-methyl-1-propene, cis-5-hydroxy-2-pentene, trans-5-hydroxy-2-pentene, cis-1,4-dihydroxy-2-butene, trans-1,4-dihydroxy-2-butene, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 2-hydroxyethyl crotonate, 2,3,4,5,6-pentahydroxyhexyl acrylate, 2,3,4,5,6-pentahydroxyhexyl methacrylate, 2,3,4,5-tetrahydroxypentyl acrylate, 2,3,4,5-tetrahydroxypentyl methacrylate, etc.

Of these, 2-hydroxyethyl methacrylate is most preferable.

These hydroxyl group-containing alkenyl monomers can be used alone or in combination of two or more.

The content of the hydroxyl group-containing alkenyl monomer is 0.01-15% by weight, preferably 0.1-5% by weight, more preferably 0.1-2% by weight, particularly preferably more than 0.1% by weight and less than 0.5% by weight, based on the total weight of the rubber-modified thermoplastic styrene resin (B)(a) and the polyamide elastomer (A). When the content of the hydroxyl group-containing alkenyl monomer is less than 0.01% by weight of the total weight of (A) and (B), the rubber-modified thermoplastic styrene resin (B)(a) has low compatibility with the polyamide elastomer (A), resulting in low impact resistance and low antistatic property. When the content is more than 15% by weight, the resulting composition has a reduced heat stability during molding as well as a reduced moldability. When the content of the hydroxyl group-containing alkenyl monomer is 0.1-2% by weight, preferably more than 0.1% by weight and less than 0.5% by weight, of the total weight of (A) and (B), the resulting composition has a better balance in respect of heat stability during molding, moldability, antistatic property and impact resistance.

In addition to the hydroxyl group-containing alkenyl monomer, it is also possible to optionally copolymerize other monomers copolymerizable with the styrene monomer. Such other monomer includes acrylonitrile, methacrylonitrile, methyl methacrylate, N-phenylmaleimide, N-cyclohexylmaleimide, etc.

When the styrene monomer is used alone in the preparation of the rubber-modified thermoplastic styrene resin (B)(a), the impact resistance becomes poor. Therefore, it is preferable to copolymerize acrylonitrile with the styrene monomer.

When the rubber-modified thermoplastic styrene resin (B)(a) contains a hydroxyl group-containing alkenyl monomer in the form of a graft copolymer, the trunk onto which the alkenyl monomer is to be grafted can be, for example, (i) a rubbery polymer, (ii) the graft layer of a graft copolymer or (iii) a non-grafted styrene polymer. Of these, (ii) and (iii) are preferable, and (iii) is particularly preferable.

The rubber-modified thermoplastic styrene resin (B)(a) can be obtained specifically by substituting the hydroxyl group-containing alkenyl monomer for a part of the monomers to be copolymerized in the preparation of a conventional styrene copolymer resin such as acrylonitrile-butadiene-styrene resin (ABS resin), acrylonitrile-ethylene-propylene-styrene resin (AES resin), methyl methacrylate-butadiene-styrene resin (MBS resin), acrylonitrile-butadiene-methyl methacrylate-styrene resin, acrylonitrile-n-butyl acrylate-styrene resin (AAS resin), rubber-modified polystyrene [high impact polystyrene (HIPS)], a heat-resistant rubber-modified styrene resin using α -methylstyrene, or the like, or substituting the hydroxyl group-containing alkenyl monomer for a part of the monomers to be copolymerized in the preparation of the styrene resin to be mixed with said styrene copolymer resin.

Of the thus obtained rubber-modified thermoplastic styrene resins (B)(a), most preferable is an ABS resin containing a hydroxyl group-containing alkenyl monomer as a copolymerized component.

The rubber-modified thermoplastic styrene resin (B)(a) used in this invention can be produced by emulsion polymerization, solution polymerization, suspension polymerization or the like.

A polymerization initiator, a molecular weight modifier, an emulsifier, a dispersing agent, a solvent and the like may be used in the above production, and they may be those which are usually used in the above polymerization methods.

The preferable process for producing a rubber-modified thermoplastic styrene resin (B)(a) comprises mixing (1) a graft copolymer obtained by graft-copolymerizing, in the presence of the rubbery polymer obtained by emulsion polymerization, the monomers using an emulsifier and a polymerization initiator, generally at a temperature of 30-150°C for 1-15 hours at a pressure of 1.0-5.0 kg/cm², provided that the graft copolymer comprises a non-grafted styrene polymer, with (2) a styrene polymer obtained by emulsion polymerization or solution polymerization.

Next, the thermoplastic polyurethane (B)(b)(1) used in this invention is obtained by uniformly mixing (P) a high molecular compound having a number-average molecular weight of 500-2,000 and two or more hydroxyl groups, (Q) a compound having two or more active hydrogen atoms and a molecular weight of 500 or more and capable of reacting with isocyanate group, and (R) an organic diisocyanate at equivalent ratios of (P) : (Q) = 1 : 0.2-4 and [(P) + (Q)] : (R) = 1.0 : 0.75-1.3 and then reacting them with heating.

If necessary, a thermoplastic polyurethane consisting of only the components (P) and (R) may be used.

As the high molecular compound (P) having two or more hydroxyl groups, there can be used polyester glycols obtained by, for example, condensation between a saturated aliphatic glycol having 2-8 carbon atoms and a saturated aliphatic dicarboxylic acid having 4-10 carbon atoms or an aromatic dicarboxylic acid, or copolymerization of an alkylene glycol with a lactone group.

As the high molecular compound (P), there can also be similarly used poly(alkylene oxide)glycols obtained by, for example, condensation of alkylene oxides having 2-4 carbon atoms, condensation of an alkylene oxide and an alkylene glycol or ring-opening polymerization of tetrahydrofuran; dihydroxypolyesteramides; dihydroxypolyacetals; and dihydroxypolyalkylenes. Particularly preferable are dihydroxypolyethylene adipate, dihydroxypolybutylene adipate, poly(tetramethylene oxide)glycol, etc.

The compound (Q) having a molecular weight of 500 or less and at least two active hydrogen atoms and capable of reacting with isocyanate group is a saturated aliphatic glycol having 2-6 carbon atoms, an alicyclic glycol such as 1,4-cyclohexylene glycol or the like, or an aromatic glycol such as 1,4-xylylene glycol, phenylene bis-(α -hydroxyethyl ether) and the like. These compounds can be used alone or in combination of two or more. A small amount of water or a trihydric alcohol (e.g. trimethylolpropane, hexanetriol, glycerine) may be used together with the above glycols.

The organic diisocyanate (R) may be any organic diisocyanate which is usually used in the production of polyurethane resin, and includes, for example, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, phenylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenylethane diisocyanate, 1,5-naphthylene diisocyanate, 3,3'-dimethylbiphenyl-4,4'-diisocyanate, 3,3'-dimethylbiphenyl-4,4'-diisocyanate, o-, m- or p-xylylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, other similar diisocyanates and their dimers. They can be used alone or in admixture of two or more. Of these organic diisocyanates, 4,4'-diphenylmethane diisocyanate is particularly preferable.

The functional group-containing styrene resin used as the (B)(b)(2) component in this invention is obtained by copolymerizing a conventional styrene resin with a compound having at least one functional group selected from the group consisting of carboxyl group, acid anhydride group, amino group, epoxy group and hydroxyl group.

The (B)(b) component of this invention is a combination of (1) the thermoplastic polyurethane and (2) the functional group-containing styrene resin. This combination may further incorporate a conventional styrene resin.

In the present specification, the styrene resin implies a resin obtained by copolymerizing, in the presence or absence of a rubbery polymer, resin-forming monomers consisting of an aromatic alkenyl compound, an alkenyl cyanide compound and, if necessary, other alkenyl monomers copolymerizable therewith.

The rubbery polymer includes, for example, copolymers of ethylene and an α -olefin, such as ethylene-propylene random or block copolymer, ethylene-butene random or block copolymer and the like; copolymers of ethylene and an unsaturated carboxylic acid ester, such as ethylene-methacrylate copolymer, ethylene-butyl acrylate copolymer and the like; copolymers of ethylene and a vinyl fatty acid ester, such as ethylene-vinyl acetate copolymer and the like; ethylene-propylene-nonconjugated diene terpolymers such as ethylene-propylene-ethylidenenorbornene terpolymer, ethylene-propylene-hexadiene terpolymer and the like; diene rubbers such as polybutadiene, polyisoprene, styrene-butadiene random or block copolymer, acrylonitrile-butadiene copolymer, butadiene-isoprene copolymer and the like; and

butylene-isoprene copolymer. They can be used alone or in combination of two or more.

Of these rubbery polymers, an ethylene-propylene rubber, an ethylene-propylene-nonconjugated diene terpolymer and a diene rubber are preferred, and a polybutadiene and a styrene-butadiene copolymer are more preferable in view of impact resistance. The styrene content in the styrene-butadiene copolymer is desirably 50% by weight or less.

The rubbery polymer content in the styrene resin is preferably 3-35% by weight, more preferably 5-35% by weight, particularly preferably 5-33% by weight. The rubbery polymer content of less than 3% by weight gives poor impact resistance, and the rubbery polymer content of more than 35% by weight gives poor moldability and high heat-shrinkage percentage.

The aromatic alkenyl compound includes styrene, α -methylstyrene, methylstyrene, vinylxylene, monochlorostyrene, dichlorostyrene, monobromostyrene, dibromostyrene, p-t-butylstyrene, ethylstyrene, vinyl-naphthalene, o-methylstyrene, dimethylstyrene, etc. These compounds can be used alone or in combination of two or more. Of these, styrene is preferable. When two or more aromatic alkenyl compounds are used, it is preferable that they contain styrene in an amount of 50% by weight or more.

The alkenyl cyanide compound includes acrylonitrile, methacrylonitrile, etc. Acrylonitrile is preferred.

Said other alkenyl compound copolymerizable with the aromatic alkenyl compound and the alkenyl cyanide compound includes, for example, alkyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, dodecyl acrylate, octadecyl acrylate and the like; aryl acrylates such as phenyl acrylate, benzyl acrylate and the like; alkyl methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, octyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, dodecyl methacrylate, octadecyl methacrylate and the like; aryl methacrylates such as phenyl methacrylate, benzyl methacrylate and the like; and maleimide compounds such as maleimide, N-methylmaleimide, N-ethylmaleimide, N-phenylmaleimide, N-o-chlorophenylmaleimide, N-cyclohexylmaleimide and the like.

These copolymerizable alkenyl compounds can be used alone or in combination of two or more.

These copolymerizable alkenyl compounds are used in an amount of preferably 50% by weight or less, more preferably 20% by weight or less, based on the weight of the styrene resin component.

The styrene resin may be a mixture of (1) a resin obtained by polymerizing resin-forming monomers in the presence of the above-mentioned rubbery polymer, with (2) a resin obtained by polymerizing resin-forming monomers in the absence of the rubbery polymer (hereinafter, the mixture is referred to as "aromatic alkenyl copolymer" in some cases).

Specific examples of the styrene resin include an acrylonitrile-butadiene rubber-styrene resin (ABS resin), an acrylonitrile-ethylene-propylene rubber-styrene resin (AES resin), an acrylonitrile-butadiene rubber-methyl methacrylate-styrene resin (ABSM resin), an acrylonitrile-styrene copolymer (AS resin), a high impact polystyrene (HIPS) and an acrylonitrile-n-butyl acrylate rubber-styrene resin (AAS resin).

The styrene resin used in this invention can be produced by emulsion-, solution- or suspension-polymerizing the above-mentioned monomers in the presence or absence of the above-mentioned rubbery polymer.

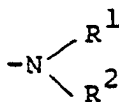
A polymerization initiator, a molecular weight modifier, an emulsifier, a dispersing agent, a solvent and the like may be used in the above polymerization and they may be those which are ordinarily used in such polymerization.

The preferable process for producing the styrene resin comprises mixing (1) a graft copolymer obtained by graft-copolymerizing, in the presence of a rubbery polymer obtained by emulsion-polymerization, the monomers using an emulsifier and a polymerization initiator, generally at a temperature of 30-150°C for 1-15 hours at a pressure of 1.0-5.0 kg/cm² (the graft copolymer includes a non-grafted styrene polymer), with (2) a styrene polymer obtained by emulsion polymerization or solution polymerization.

The functional group-containing unsaturated compound to be copolymerized with the styrene resin includes, as carboxyl group-containing unsaturated compound, for example, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, itaconic acid, maleic acid and the like. Acrylic acid and methacrylic acid are preferred. These compounds can be used alone or in combination of two or more.

The acid anhydride group-containing unsaturated compound constituting the functional group-containing styrene resin (B)(b)(2) includes maleic anhydride, itaconic anhydride, chloromaleic anhydride, citraconic anhydride, butenylsuccinic anhydride, tetrahydrophthalic anhydride, etc. Of these, maleic anhydride is preferable. These compounds can be used alone or in combination of two or more.

The amino group-containing unsaturated compound constituting the functional group-containing styrene resin (B)(b)(2) is an alkenyl monomer having at least one amino or substituted amino group represented by the following formula:



wherein R¹ is a hydrogen atom, a methyl group or an ethyl group and R² is a hydrogen atom, an alkyl group having 1-12 carbon atoms, an alkanoyl group having 2-12 carbon atoms, a phenyl group having 6-12 carbon atoms, a cycloalkyl group having 6-12 carbon atoms or a derivative thereof. The amino group-containing unsaturated compound includes, for example, derivatives of alkyl acrylates and methacrylates, such as aminoethyl acrylate, propylaminoethyl acrylate, dimethylaminoethyl methacrylate, aminopropyl methacrylate, phenylaminoethyl methacrylate, cyclohexylaminoethyl methacrylate and the like; derivatives of vinylamine such as N-vinyldiethylamine, N-acetylvinyllamine and the like; derivatives of allylamine such as allylamine, N-methylallylamine and the like; derivatives of acrylamide such as acrylamide, N-methylacrylamide and the like; and aminostyrene such as p-aminostyrene and the like.

Of these, allylamine, aminoethyl methacrylate, aminopropyl methacrylate and aminostyrene are particularly preferable because they are economically available on a commercial scale.

These amino or substituted amino group-containing unsaturated compounds can be used alone or in combination of two or more.

The epoxy group-containing unsaturated compound constituting the functional group-containing styrene resin (B)(b)(2) is a compound having, in the molecule, an epoxy group and an unsaturation copolymerizable with an olefin or an ethylenically unsaturated compound.

Specific examples of the epoxy group-containing unsaturated compound are glycidyl acrylate, glycidyl methacrylate, glycidyl itaconate, glycidyl butenecarboxylate, allyl glycidyl ether, 2-methylallyl glycidyl ether, styrene-p-glycidyl ether, 3,4-epoxybutene, 3,4-epoxy-3-methyl-1-butene, 3,4-epoxy-1-pentene, 3,4-epoxy-3-methylpentene, 5,6-epoxy-1-hexene, vinylcyclohexene monooxide and p-glycidylstyrene. These epoxy group-containing unsaturated compounds can be used alone or in combination of two or more.

The hydroxyl group-containing unsaturated compound constituting the functional group-containing styrene resin (B)(b)(2) includes the same hydroxyl group-containing alkenyl compounds as used in the (B)-(a) component.

The hydroxyl group-containing unsaturated compound can be used alone or in combination of two or more.

The amount of the functional group-containing unsaturated compound used is 0.01-15% by weight, preferably 0.05-10% by weight, more preferably 0.1-5% by weight, based on the weight of the thermoplastic resin composition of this invention.

When the amount of the functional group-containing unsaturated compound is less than 0.01% by weight, the resulting (B) component has low compatibility with the polyamide elastomer (A) and consequently the final thermoplastic resin composition has low impact resistance and low antistatic property. When the amount is more than 15% by weight, the composition obtained has low heat stability during molding and low moldability.

The base material used when the functional group-containing unsaturated compound is copolymerized with the styrene resin to form a functional group-containing styrene resin (B)(b)(2), is (1) a rubbery polymer, (2) the graft layer of a graft copolymer or (3) a non-grafted styrene polymer. Of these, (2) or (3) is preferable.

The functional group-containing styrene resin can be produced by substituting the above-mentioned functional group-containing unsaturated compound for a part of the monomers in the production of a conventional styrene resin such as acrylonitrile-butadiene-styrene resin (ABS resin), acrylonitrile-ethylene-propylene-styrene resin (AES resin), methyl methacrylate-butadiene-styrene resin (MBS resin), acrylonitrile-butadiene-methyl methacrylate-styrene resin, acrylonitrile-n-butyl acrylate-styrene resin (AAS resin), rubber-modified polystyrene (high-impact polystyrene, HIPS), acrylonitrile-styrene resin (AS resin), methyl methacrylate-styrene resin (MS resin) or the like.

The most preferable functional group-containing styrene resin is a resin obtained by copolymerizing a carboxyl group- or acid anhydride group-containing unsaturated compound with ABS resin-forming components.

The thermoplastic resin composition of this invention comprises, as the main components, (A) a polyamide elastomer and (B)(a) a hydroxyl group-containing rubber-modified thermoplastic styrene resin and/or (b)(1) a thermoplastic polyurethane and (2) a functional group-containing styrene resin. The proportion of the (A) component is 1-90% by weight, preferably 5-60% by weight, more preferably 7-40%

by weight and the proportion of the (B) component is 10-99% by weight, preferably 40-95% by weight, more preferably 60-93% by weight.

When the proportion of the polyamide elastomer (A) is less than 1% by weight, the resulting thermoplastic resin composition is insufficient in moldability, antistatic property and impact strength. When the proportion is more than 90% by weight, the composition is flexible and has poor mechanical properties.

When the thermoplastic resin composition of this invention comprises the (A) component and the (B) component, the compounding proportion of the polyamide elastomer (A) to the thermoplastic polyurethane (B)(b)(1) is such that the amount of the (A) component is 1-90% by weight, preferably 30-85% by weight and the amount of the (B)(b)(1) component is 99-10% by weight, preferably 70-15% by weight [(A) + (B)(b)(1) = 100% by weight].

The compounding proportion of the total amount of [(A) + (B)(b)(1)] to the aromatic alkenyl copolymer containing the functional group-containing styrene resin (B)(b)(2) is such that the amount of the (A) component plus the (B)(b)(1) component is 1-90% by weight, preferably 5-30% by weight and the amount of the (B)(b)(2) component is 99-10% by weight, preferably 95-70% by weight. When the total amount of (A) and (B)(b)(1) is less than 1% by weight, the resulting composition has low antistatic property. When the total amount is more than 90% by weight, the composition is flexible and has poor mechanical properties.

The composition of this invention can further comprise (C) a styrene resin, in addition to the (A) and (B) components, when the (B) component consists of the (B)(b) component.

The styrene resin (C) is the same as mentioned in the (B)(b) component.

When the present thermoplastic resin composition comprises the (A) component, the (B)(b) component and the (C) component, the preferable amounts of these components compounded are as follows:

The compounding proportion of the polyamide elastomer (A) to the styrene resin (C) is such that the amount of the (A) component is 1-90% by weight, preferably 5-30% by weight and the amount of the (C) component is 99-10% by weight, preferably 95-70% by weight [(A) + (C) = 100% by weight]. When the amount of the (A) component is less than 1% by weight, the resulting composition has insufficient antistatic property. When the amount of the (A) component is more than 90% by weight, the composition is flexible.

The compounding proportion of the thermoplastic polyurethane (B)(b)(1) to the functional group-containing styrene resin (B)(b)(2) is such that the amount of the (B)(b)(1) component is 40-99% by weight, preferably 50-90% by weight and the amount of the (B)(b)(2) component is 60-1% by weight, preferably 50-10% by weight [(B)(b)(1) + (B)(b)(2) = 100% by weight]. When the amount of the (B)(b)(1) component is less than 40% by weight, the resulting composition has poor impact strength. When the amount of the (B)(b)(1) component is more than 99% by weight, the compatibility between the polyamide elastomer (A) and the styrene resin (C) is poor and the resulting composition is inferior in mechanical properties (e.g. impact strength).

The proportion of the (B)(b) component in the present composition containing the (C) component is 0.1-50 parts by weight, preferably 1-30 parts by weight, per 100 parts by weight of [(A) + (C)]. When the proportion is less than 0.1 part by weight, the compatibility between the polyamide elastomer (A) and the styrene resin (C) is poor and the resulting composition is inferior in mechanical properties (e.g. impact strength). When the proportion is more than 50 parts by weight, the composition is flexible and has inferior mechanical properties.

The thermoplastic resin composition of this invention can be obtained by mixing the (A) component, the (B) component and, if necessary, the (C) component by a conventional method. For example, these components are mixed by a mixer, and melt kneaded at 200-280 °C and pelletized by an extruder. Simply, these components are melt kneaded in a molding machine to obtain a molded article in one step.

When the (B)(b) component is used as the (B) component, the thermoplastic polyurethane (B)(b)(1) and the functional group-containing styrene resin (B)(b)(2) are reacted with each other with melt-kneading to obtain a reaction product; the reaction product is then mixed with the polyamide elastomer (A) and, if necessary, the styrene resin (C) by an ordinary method, thereby a composition with excellent physical properties can be obtained.

The melt-kneading of the (B)(b)(1) component and the (B)(b)(2) component to react them, thereby obtaining a reaction product can be effected by, for example, mixing the components by a mixer and melt-kneading them at 180-250 °C by an extruder. Simply, all the components are melt-kneaded in a molding machine to obtain a molded article in one step. In other melt-kneading methods, a styrene resin and a thermoplastic polyurethane are melt-kneaded in the presence of a functional group-containing unsaturated compound. In these melt-kneading methods, an organic peroxide may be used.

The composition of this invention comprises (A) and (B) as the main components. The composition can further comprise ordinary synthetic resins and elastomers such as vinyl chloride resin, polyolefin resin, polybutylene terephthalate, polyethylene terephthalate, polycarbonate, polyphenylene ether, styrene

elastomer, polyester elastomer, polyamide, polysulfone, polyacetal, polyphenylene sulfide, polyarylate, fluoro-resin, liquid crystal polymer and the like, in an amount of about 50% by weight or less.

The composition of this invention can further comprise various compounding agents.

The compounding agents include, for example, antioxidants such as 2,6-di-t-butyl-4-methylphenol, 2-(1-methylcyclohexyl)-4,6-dimethylphenol, 2,2-methylene-bis-(4-ethyl-6-t-butylphenol), 4,4'-thiobis-(6-t-butyl-3-methylphenol), dilaurylthio dipropionate, tris-(dinonylphenyl) phosphite and the like; ultraviolet absorbers such as p-t-butylphenyl salicylate, 2,2'-dihydroxy-4-methoxybenzophenone, 2-(2'-hydroxy-4'-n-octoxyphenyl)benzotriazole and the like; lubricants such as paraffin wax, stearic acid, hardened oil, stearamide, methylene-bis(stearamide), n-butyl stearate, ketone wax, octyl alcohol, lauryl alcohol, triglyceride of hydroxystearic acid and the like; flame retardants such as antimony oxide, ammonium hydroxide, zinc borate, tricresyl phosphate, tris(dichloropropyl) phosphate, chlorinated paraffin, tetrabromobutane, hexabromobenzene, tetrabromobisphenol A and the like; antistatic agents such as stearamidopropyl dimethyl- β -hydroxyethyl ammonium nitrate and the like; coloring agents such as titanium oxide, carbon black and the like; fillers such as calcium carbonate, clay, silica, glass fiber, glass beads, carbon fiber and the like; pigments; and the like.

The thermoplastic resin composition of this invention has an antistatic property, is superior in mechanical properties, heat resistance during molding, moldability and surface appearance, and is useful in applications such as housings for office automation equipment (these equipment has had electrostatic problems), chassis, housings for optical or magnetic media, cases for accommodating various goods, trays used in the course of electronic parts production, containers, and exterior parts for home electric appliances (some of these appliances collect dust, etc. and give poor appearance during the use).

The composition of this invention further has very high heat stability and, even when molded at high temperatures or allowed to reside during molding, gives only small reduction in impact resistance, gloss and antistatic property. Accordingly, the composition gives only small change in quality when molded under severe conditions to meet recent diversified applications, and is very useful in industry.

This invention is hereinafter explained more specifically referring to Examples. In the Examples, parts and % are by weight unless otherwise specified.

Reference Example 1 (Preparation of rubber-modified styrene polymers G-1 and G-2)

Into a 7-liter glass flask provided with a stirrer were batchwise fed the chemicals shown in the upper column of Table 1. The air in the flask was replaced with a nitrogen gas, and the interior temperature of the flask was elevated to 40 °C while maintaining the jacket of the flask at 70 °C.

Then, to the flask contents were added 0.3 part of sodium pyrophosphate dissolved in 10 parts of water, 0.35 part of dextrose, 0.01 part of ferrous sulfate and 0.1 part of cumene hydroperoxide, and polymerization was initiated.

One hour after the start of the polymerization, the incremental mixture shown in the lower column of Table 1 was added continuously over 3 hours. The polymerization were continued for a further 1 hour, whereby the polymerization was almost completed.

To the graft copolymer (rubber-modified styrene polymer) latex thus obtained was added, as an antioxidant, 1.0 part of 2,6-t-butyl-p-cresol. Then, sulfuric acid was added in a proportion of 2 parts per 100 parts of the polymer, to coagulate the latex at 90 °C.

The resulting coagulum was separated, water-washed, dehydrated and dried to obtain rubber-modified styrene polymers G-1 and G-2.

Table 1

Chemicals (parts)		G-1	G-2
Batchwise feed			
Polybutadiene latex ^{*1} (in terms of solid content)		32	32
Styrene-butadiene copolymer latex ^{*2} (in terms of solid content)		8	8
Styrene		14	12.7
Acrylonitrile		6	5.1
2-Hydroxyethyl acrylate		-	2.2
t-Dodecylmercaptan		0.15	0.15
Potassium rosinat		0.5	0.5
Potassium hydroxide		0.01	0.01
Deionized water		100	100
Incremental mixture			
Styrene		28	25.5
Acrylonitrile		12	10.1
2-Hydroxyethyl acrylate		-	4.4
t-Dodecylmercaptan		0.3	0.3
Potassium rosinat		1.0	1.0
Potassium hydroxide		0.02	0.02
Cumene hydroperoxide		0.1	0.1
Deionized water		50	50
Note:			

*1 #0700 manufactured by Japan Synthetic Rubber Co., Ltd.

*2 #0561 manufactured by Japan Synthetic Rubber Co., Ltd.

Reference Example 2 (Preparation of styrene polymers M-1 to M-9)

In a 7-liter glass flask provided with a stirrer were placed the chemicals shown in Table 2. The air in the flask was replaced with a nitrogen gas, and the interior temperature of the flask was elevated to 50 °C while maintaining the jacket of the flask at 70 °C.

Then, to the flask contents were added 0.3 part of potassium persulfate dissolved in 4 parts of water and 0.1 part of sodium sulfite dissolved in 1 part of water, and they were subjected to copolymerization for 3 hours.

To the resulting styrene polymer latex was added calcium chloride in a proportion of 2 parts per 100 parts of the polymer to coagulate the latex at 90 °C. The resulting coagulum was separated, water-washed, dehydrated and dried to obtain styrene polymers M-1 to M-9 shown in Table 2.

Table 2

	Chemicals (parts)	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	M-9
5	Styrene	71.25	67.5	60	37.5	60	67.5	70.5	66.5	80
	Acrylonitrile	23.75	22.5	20	12.5	20	22.5	23.5	19.5	-
	2-Hydroxyethyl methacrylate	5	10	20	50	-	-	-	10	20
	2-Hydroxypropyl methacrylate	-	-	-	-	20	-	-	-	-
	Acrylamide	-	-	-	-	-	10	-	-	-
10	Methacrylic acid	-	-	-	-	-	-	6	-	-
	t-Dodecylmercaptan	0.3	0.3	0.3	0.1	0.3	0.3	0.3	0.3	0.3
	Sodium dodecylbenzenesulfonate	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Deionized water	250	250	250	400	250	400	250	250	250
	Methyl methacrylate	-	-	-	-	-	-	-	2	-
15	n-Butyl methacrylate	-	-	-	-	-	-	-	2	-

20 Reference Example 3 (Preparation of rubber-modified styrene polymer G-3)

A 65-liter stainless steel reactor provided with a paddle type stirrer was purged with a nitrogen gas. Thereinto were charged 24 parts of an EPDM (JSR EP 24 manufactured by Japan Synthetic Rubber Co., Ltd.) having an iodine value of 15, a Mooney viscosity of 65 and a propylene content of 43% and containing ethyldidenenorbornene as a diene component, 56 parts of styrene, 20 parts of acrylonitrile and 100 parts of toluene. The mixture was stirred at 50 °C until the rubber dissolved completely. Then, there were added 0.1 part of t-dodecylmercaptan, 0.2 part of dibenzoyl peroxide, 0.2 part of t-butylperoxy-1-propyl carbonate and 0.1 part of dicumyl peroxide. Thereafter, they were subjected to polymerization at 80 °C for 3 hours, at 100 °C for 3 hours and at 125 °C for 3 hours in this order (total 9 hours).

30 The unreacted monomers and the solvent were removed by steam distillation. The residue was ground and dried to obtain a polymer.

35 Examples 1-13 and Comparative Examples 1-8

There were used, as the rubber-modified styrene resin (B), the rubber-modified styrene polymers G-1 and G-2 obtained in Reference Example 1, the styrene polymers M-1 to M-7 obtained in Reference Example 2, the rubber-modified styrene polymer G-3 obtained in Reference Example 3, G-4 (Toporex HI 800 manufactured by Mitsui Toatsu Chemicals, Inc.) and a styrene-acrylonitrile copolymer resin (AS resin) (AS-240 manufactured by Japan Synthetic Rubber Co., Ltd. having a bound acrylonitrile content of 24.5% and $[\eta]$ in methyl ethyl ketone at 30 °C of 0.60) and, as the polyamide elastomer (A), PAE-A (PEBAX 4011 manufactured by Atochem Co. comprising a polyethylene glycol as a polyether component), PAE-B (PEBAX 5533 manufactured by Atochem Co. comprising tetramethylene glycol as a polyether component) and PA-A (Capron 8200, a trade name of Allied Chemical Corp. for nylon 6). These components were mixed with the compounding recipe shown in Table 3, using a Henschel mixer.

Each of the resulting mixtures was passed through a 50-mmØ twin-screw vented extruder at 230 °C for pelletization. The resulting pellets were dried at 90 °C, subjected to injection molding at 230 °C, then measured for the physical properties shown in Table 3.

50 A test piece for evaluation of thermal stability of Izod impact strength or gloss was prepared as follows: Using an injection machine, a test piece was firstly prepared at a molding temperature of 230 °C in a 1-minute cycle for evaluation of Izod impact strength or gloss. Then, this test piece was fed into the cylinder, allowed to stand (reside) for 10 minutes as it was, and molded in a 1-minute cycle to obtain an "after residence" test piece.

55 A test piece for evaluation of thermal stability of antistatic property was prepared as follows. Using an injection machine, a disc of 100 mm in diameter and 2 mm in thickness was prepared at molding temperature of 230 °C or 270 °C in a 1-minute molding cycle.

The physical properties shown in Table 3 were measured in accordance with the following methods:

Melt flow rate was measured by ASTM D 1238 (220 °C).

Heat distortion temperature was measured by ASTM D 648 (load: 18.6 kg/cm², no annealing).

Izod impact strength was measured by ASTM D 256 (notched).

Gloss was measured by ASTM D 523 (3 mm thick-ness).

Antistatic property was evaluated by measuring the surface resistivity. That is, the disc prepared above
5 at 230 °C or 270 °C was molded at a relative humidity of 50% at an environmental temperature of 23 °C,
and the molded article was subjected to 24-hour conditioning and then measured for surface resistivity
using an ultra-insulation resistance meter (4329 Type manufactured by Yokokawa-Hewlett Packard Co.).
Also, the disc prepared at 230 °C was allowed to stand, after the completion of the above measurement, at
a relative humidity of 50% at an environmental temperature of 23 °C for one month, washed with a solvent
10 to remove the water present on the surface, subjected again to 24-hour conditioning, and then measured for
surface resistivity in the same manner.

As is clear from Table 3, the thermoplastic resin compositions of Examples 1-13 are those of this
invention and all superior in heat stability during molding, mechanical properties, moldability and antistatic
property, as aimed at in this invention.

15 Meanwhile, the thermoplastic resin composition of Comparative Example 1 comprising no polyamide
elastomer (A) is outside the scope of this invention and inferior in antistatic property and moldability. The
thermoplastic resin composition of Comparative Example 2 comprises a rubber-modified thermoplastic
styrene resin containing no hydroxyl group-containing alkenyl monomer and is inferior in impact resistance.

20 The thermoplastic resin composition of Comparative Example 3 comprises a rubber-modified thermo-
plastic styrene resin in an amount larger than required in this invention and is inferior in moldability and
antistatic property.

The composition of Comparative Example 4 comprises a rubber-modified thermoplastic styrene resin in
an amount smaller than required in this invention and is rubbery and not a resin. The thermoplastic resin
composition of Comparative Example 5 uses a carboxyl group-containing alkenyl monomer in place of the
25 hydroxyl group-containing alkenyl monomer and is inferior in heat stability.

The thermoplastic resin composition of Comparative Example 6 uses acrylamide in place of the
hydroxyl group-containing alkenyl monomer and is inferior in heat stability. The thermoplastic resin
compositions of Comparative Examples 7 and 8 use a polyamide resin (nylon) in place of the polyamide
elastomer and are inferior in antistatic property.

30

35

40

45

50

55

Table 3

	Example			
	1	2	3	4
Compounding recipe (parts)				
(B) (a) Component				
Rubber-modified styrene polymer G-1	30	30	30	30
G-2	-	-	-	-
G-3	-	-	-	-
G-4	-	-	-	-
(C) Component				
Styrene polymer M-1	-	10	-	-
M-2	-	-	10	-
M-3	1	-	-	10
M-4	-	-	-	-
M-5	-	-	-	-
M-8	-	-	-	-
M-9	-	-	-	-
AS resin AS-240	57	48	48	48
(A) Component				
PAE-A	12	12	12	12
PAE-B	-	-	-	-
PA-A	-	-	-	-

(to be cont'd.)

Table 3 (Cont'd.)

5	10	15	20	25	30	35	40	45	50	55
5	6	7	8	9	10	11	12	13		
-	30	30	30	30	-	30	28	-		
-	-	-	-	-	30	-	-	-		
30	-	-	-	-	-	-	-	-		
-	-	-	-	-	-	-	-	78		
-	-	10	10	10	-	10	-	-		
-	-	-	-	-	-	-	-	-		
1	1	-	-	-	-	-	-	-		
-	-	-	-	-	10	-	-	-		
-	-	-	-	-	-	-	5	-		
-	-	-	-	-	-	-	-	10		
64	59	35	20	48	48	48	55	-		
5	10	25	40	12	12	-	12	12		
-	-	-	-	-	-	12	-	-		
-	-	-	-	-	-	-	-	-		

(to be cont'd.)

Table 3 (Cont'd.)

Proportion of each component in composition (%)				
(B) and (C) components	88	88	88	88
(A) Component	12	12	12	12
Hydroxyl or other functional group- containing alkenyl monomer	0.2	0.5	1.0	2.0
Physical properties				
Melt flow rate (g/10 min)	32	26	27	19
Heat distortion temperature (°C)	95	94	93	93
Izod impact strength (notched) (Kg-cm/cm)	25	31	36	40
Izod impact strength (after residence, 230°C x 10 min) (Kg-cm/cm)	19	23	25	26
Retention of impact strength after residence (%)	76	74	70	65
Gloss (%)	88	87	87	86
Gloss (after residence, 230°C x 10 min) (%)	83	82	81	76
Retention of gloss after residence (%)	94	94	93	88
Surface resistivity (230°C) (Ω)	3×10^{10}	1×10^{10}	1×10^{10}	1×10^{10}
Surface resistivity (after being allowed to stand for one month and subsequently washed) (Ω)	3×10^{10}	1×10^{10}	1×10^{10}	1×10^{10}
Surface resistivity (270°C) (Ω)	3×10^{10}	1×10^{10}	1×10^{10}	2×10^{10}

(to be cont'd.)

Table 3 (Cont'd.)

95	90	75	60	88	88	88	88	88
5	10	25	40	12	12	12	12	12
0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	2.0
17	22	25	30	27	26	26	28	70
96	94	84	78	93	94	93	93	72
14	29	50	55	30	32	34	32	8
11	2	35	39	23	24	25	23	5
79	74	70	71	77	75	74	72	63
91	89	87	84	87	87	87	86	70
85	83	81	79	81	81	83	81	65
93	93	93	94	93	93	95	94	93
3x10 ¹²	2x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	2x10 ¹²	1x10 ¹⁰	1x10 ¹¹
8x10 ¹²	2x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	2x10 ¹²	1x10 ¹⁰	1x10 ¹¹
4x10 ¹²	2x10 ¹⁰	2x10 ¹⁰	2x10 ¹⁰	1x10 ¹⁰	1x10 ¹⁰	2x10 ¹²	1x10 ¹⁰	1x10 ¹¹

Table 3 (Continued)

	1	2	3
Compounding recipe (parts)			
(B) (a) Component			
Rubber-modified styrene polymer G-1	30	30	30
G-2	-	-	-
G-3	-	-	-
(C) Component			
Styrene polymer M-1	-	-	10
M-2	-	-	-
M-3	-	-	-
M-4	-	-	-
M-5	-	-	-
M-6	-	-	-
M-7	-	-	-
AS resin AS-240	70	58	59.5
(A) Component			
PAE-A	-	12	0.5
PAE-B	-	-	-
PA-A	-	-	-

(to be cont'd.)

Comparative Example

4	5	6	7	8
-	30	30	30	30
-	-	-	-	-
-	-	-	-	-
-	-	-	10	10
5	-	-	-	-
-	-	-	-	-
-	-	-	-	-
-	-	5	-	-
-	10	-	-	-
-	48	53	48	20
95	12	12	-	-
-	-	-	-	-
-	-	-	12	40

(to be cont'd.)

Table 3 (Cont'd.)

Proportion of each component in composition (%)				
(B) and (C) components		100	88	99.5
(A) Component		-	12	0.5
Hydroxyl or other functional group-containing alkenyl monomer		-	-	0.5
Physical Properties				
Melt flow rate (g/10 min)		14	22	13
Heat distortion temperature (°C)		94	92	94
Izod impact strength (notched) (Kg·cm/cm)		24	11	21
Izod impact strength (after resistance, 230°C x 10 min) (Kg·cm/cm)		21	8	16
Retention of impact strength after residence (%)		88	72	76
Gloss (%)		91	86	87
Gloss (after residence, 230°C x 10 min) (%)		85	80	81
Retention of gloss after residence (%)		93	93	93
Surface resistivity (230°C) (Ω)		> 1x10 ¹⁶	1x10 ¹³	> 1x10 ¹⁶
Surface resistivity (after being allowed to stand for one month and subsequently washed) (Ω)		> 1x10 ¹⁶	1x10 ¹³	> 1x10 ¹⁶
Surface resistivity (270°C) (Ω)		> 1x10 ¹⁶	2x10 ¹³	> 1x10 ¹⁶

Table 3 (Cont'd.)

5					
10					
15					
20					
25	5	88	88	88	60
	95	12	12	12	40
	0.5	0.5	0.5	0.5	0.5
	50	25	23	18	28
	50	93	93	95	94
	Not broken	22	16	25	15
	Not broken	10	10	18	11
	100	45	63	72	71
	81	84	85	82	86
	60	32	41	75	72
	74	38	48	85	84
	6×10^9	8×10^{10}	3×10^{11}	4×10^{14}	2×10^{14}
	1×10^{10}	8×10^{10}	1×10^{10}	1×10^{15}	9×10^{14}
	2×10^{10}	7×10^{12}	2×10^{10}	1×10^{15}	2×10^{15}

Examples 14-21 and Comparative Examples 9-15

Preparation of thermoplastic polyurethanes

(1)-1: Takelac T-890 (a produce of Takeda Chemical Industries, Ltd.) was used.

(1)-2: Takelac T-155D (a product of Takeda Chemical Industries, Ltd.) was used.

(1)-3: Takelac T-498 (a product of Takeda Chemical Industries, Ltd.) was used.

Preparation of functional group-free styrene resins

(2)-1: A graft copolymer composed of 41.5 parts of a polybutadiene, 43.5 parts of styrene and 15 parts of acrylonitrile was obtained according to a conventional emulsion polymerization method.

(2)-2: A graft copolymer composed of 32 parts of an EPDM (EP 82 manufactured by Japan Synthetic Rubber Co., Ltd.), 44 parts of styrene and 24 parts of acrylonitrile was obtained according to a conventional solution polymerization method.

(2)-3: A copolymer composed of 68.5 parts of styrene and 31.5 parts of acrylonitrile was obtained according to a conventional solution polymerization method.

Preparation of functional group-containing styrene resins

(2)-4: A graft copolymer composed of 40 parts of a polybutadiene, 42 parts of styrene, 15 parts of acrylonitrile and 3 parts of acrylic acid was obtained according to a conventional emulsion polymerization method.

(2)-5: A copolymer composed of 47 parts of styrene, 25 parts of α -methylstyrene, 18 parts of acrylonitrile and 10 parts of acrylic acid was obtained according to a conventional emulsion polymerization

method.

(2)-6: A copolymer composed of 90 parts of methyl methacrylate and 10 parts of maleic anhydride was obtained according to a conventional solution polymerization method.

(2)-7: A copolymer composed of 60 parts of styrene, 20 parts of acrylonitrile and 20 parts of 2-hydroxyethyl acrylate was obtained according to a conventional emulsion polymerization method.

(2)-8: A copolymer composed of 10 parts of a polybutadiene, 63 parts of styrene, 26 parts of acrylonitrile and 1 part of methacrylic acid was obtained according to a conventional emulsion polymerization method.

The above components were mixed using a Henschel mixer with the compounding recipe shown in Table 4.

Each of the resulting mixtures was melt-kneaded at 230 °C using a 50-mmØ twin-screw vented extruder to prepare pellets. The pellets were measured for melt flow rate in accordance with JIS K 7210 (220 °C, 10 kg).

The above pellets were subjected to injection molding at 230 °C using an injection machine IS-80A (a product of Toshiba Machine Co., Ltd.) to prepare test pieces. The test pieces were measured for Izod impact strength (ASTM D 256, 1/4 in. notched, 23 °C), thermal distortion temperature (ASTM D 68, 18.6 kg/cm², 1/2 in.), flexural modulus of elasticity (ASTM D 790) and tensile strength (ASTM D 638, drawing speed = 15 mm/min).

The above pellets were also treated by an injection machine (IS-25EP, a product of Toshiba Machine Co., Ltd.) at 230 °C to prepare a disc (diameter = 100 mm, thickness = 2 mm). The disc was molded at a relative humidity of 50% at an environmental temperature of 23 °C. The molded article was subjected to 24-hour conditioning or allowed to stand for one month and washed with a detergent, and then measured for surface resistivity using an ultra-insulation resistance meter (4329A manufactured by Yokokawa-Hewlett Packard Co.).

As is clear from Table 4, the thermoplastic resin compositions of Examples 14-21 are all those of this invention and are superior in fluidity, heat resistance and mechanical strengths. Further, they have a low surface resistivity which is not much changed with the lapse of time or by surface washing, and thus have excellent antistatic property.

In contrast, in the case of the thermoplastic resin compositions of Comparative Examples 9 and 13 wherein the content of the thermoplastic polyurethane (B)(b)(1) is less than 1%, the Izod impact strength is low; and in the case of the thermoplastic resin compositions of Comparative Examples 10 and 14 wherein the content of the polyamide elastomer (A) is less than 1%, the surface resistivity is high and accordingly the antistatic property is poor.

In the case of the thermoplastic resin compositions of Comparative Examples 11 and 12 wherein a styrene resin was used without being modified with a functional group-containing compound, the Izod impact strength is low.

In the thermoplastic resin compositions of Comparative Example 15 wherein the proportion of the (A) component is less than 1% of the total of the (A) and (B) components, surface resistivity is high, in other words, antistatic property is poor.

Table 4

	Example		
	14	15	16
Compounding recipe (Parts)			
(A) Component			
Polyamide elastomer PAE-A	12	3	-
PAE-B	-	-	20
(B) (b) (1) Component			
Thermoplastic polyurethane (1)-1	3	12	-
(1)-2	-	-	1
(1)-3	-	-	-
(B) (b) (2) Component			
Functional group-free styrene resin	28	28	25
(2)-1	-	-	-
(2)-2	-	-	-
(2)-3	55	55	50
Functional group-containing styrene resin	2	2	-
(2)-4	-	-	4
(2)-5	-	-	-
(2)-6	-	-	-
(2)-7	-	-	-
(2)-8	-	-	-

- Cont'd. -

Table 4 (Cont'd.)

17	18	19	20	21	9	10
5	5	20	2	40	15	-
-	-	-	-	-	-	-
5	-	-	40	5	-	15
-	-	40	-	-	-	-
-	1	-	-	-	-	-
-	40	-	-	-	28	28
40	-	-	-	-	-	-
55	50	36	53	-	55	55
-	-	4	-	-	2	2
-	-	-	-	-	-	-
5	-	-	-	-	-	-
-	6	-	5	-	-	-
-	-	-	-	55	-	-

- to be cont'd. -

Table 4 (Cont'd.)

Comparative Example					
11	12	13	14	15	
-	12	-	0.3	0.4	
20	-	20	-	-	
-	3	-	41.7	0.4	
1	-	0.1	-	-	
-	-	-	-	-	
25	-	26	-	34	
-	35	-	-	-	
54	50	50	53	60	
-	-	-	-	-	
-	-	4	-	-	
-	-	-	-	6	
-	-	-	5	-	
-	-	-	-	-	

Table 4

Physical Properties				
Melt flow rate (g/10 min)	24	26	23	
Izod impact strength (Kg·cm/cm)	37	46	52	
Heat distortion temperature (°C)	92	92	90	
Flexural modulus (Kg/cm ²)	25,000	25,000	23,000	
Tensile strength (Kg/cm ²)	420	430	400	
Surface resistivity (Ω)				
After one day	1x10 ¹⁰	2x10 ¹²	8x10 ¹¹	
After being allowed to stand for one month and subsequently washed	1x10 ¹⁰	3x10 ¹²	9x10 ¹¹	

- to be cont'd. -

Table 4 (Cont'd.)

35	12	60	55	60	21	25
35	29	Not broken	Not broken	Not broken	18	40
93	94	70	85	85	92	92
25,000	26,000	1,100	18,000	16,000	25,000	25,000
450	460	220	300	250	400	400
1×10^{12}	2×10^{12}	1×10^9	9×10^{11}	1×10^9	1×10^{10}	6×10^{14}
1×10^{12}	3×10^{12}	1×10^9	8×10^{11}	1×10^9	1×10^{10}	9×10^{14}

- to be cont'd. -

Table 4 (Cont'd.)

25	32	31	56	16
11	12	22	Not broken	35
90	92	90	85	93
23,000	25,000	23,000	18,000	28,000
380	410	390	380	450
6×10^{12}	3×10^{11}	7×10^{12}	1×10^{13}	$> 1 \times 10^{16}$
7×10^{12}	3×10^{11}	7×10^{12}	2×10^{13}	$> 1 \times 10^{16}$

Examples 22-34 and Comparative Examples 16-25

The above-mentioned (1) components and the above-mentioned (2) components were mixed using a mixer with the compounding recipe shown in Table 5. Each of the resulting mixtures was melt kneaded at 200°C using an extruder to give rise to crosslinking reaction, thereby obtaining reaction products (b-1) to (b-6).

Table 5

	b-1	b-2	b-3	b-4	b-5	b-6
Compounding recipe (parts)						
(1)-1	50	50	50	.	.	80
(1)-2	.	.	.	50	.	.
(1)-3	50	.
(2)-4	50	.	.	50	50	20
(2)-5	.	50
(2)-6	.	.	50	.	.	.

Each of the reaction products was mixed with other components using a Henschel mixer with the compounding recipe shown in Table 6.

Each of the resulting mixtures was melt-kneaded at 230 °C using a 50-mmØ twin screw vented extruder to prepare pellets. The pellets were measured for melt flow rate in accordance with JIS K 7210 (220 °C, 10 kg).

The above pellets were subjected to injection molding at 230 °C using an injection machine IS-80A (a product of Toshiba Machine Co., Ltd.) to prepare test pieces. The test pieces were measured for Izod impact strength (ASTM D 256, 1/4 in. notched, 23 °C), thermal distortion temperature (ASTM D 68, 18.6 kg/cm², 1.2 in.), flexural modulus (ASTM D 790) and tensile strength (ASTM D 638, drawing speed = 15 mm/min).

The above pellets were also treated by an injection machine (IS-25EP, a product of Toshiba Machine Co., Ltd.) at 230 °C to prepare a disc (diameter = 100 mm, thickness = 2 mm). The disc was molded at a relative humidity of 50% at an environmental temperature of 23 °C. The molded article was subjected to 24-hour conditioning or allowed to stand for one month and washed with a detergent, and then measured for surface resistivity using an ultra-insulation resistance meter (4329A manufactured by Yokokawa-Hewlett Packard Co.). Using the same test piece, surface appearance was evaluated visually. The evaluation criteria were O (good), Δ (slightly poor) and X (very poor).

As is clear from Table 6, the thermoplastic resin compositions of Examples 22-34 are all those of this invention and are superior in fluidity, heat resistance, mechanical strengths and surface appearance. Further, they have a low surface resistivity which is not much changed with the lapse of time or by surface washing, and thus have excellent antistatic property.

In contrast, in the case of the thermoplastic resin compositions of Comparative Examples 16, 18 and 22 wherein the content of the reaction product of a thermoplastic polyurethane (1) and a functional group-containing styrene resin (2) is less than 0.1 part, the Izod impact strength is low and the surface resistivity is high (the antistatic property is poor).

In the case of the thermoplastic resin compositions of Comparative Examples 19-22 in which only a functional group-containing styrene resin (B)(b)(1) is used as the (B) component, the impact resistance and the surface appearance are poor.

In the case of the thermoplastic resin compositions of Comparative Examples 23 and 25 wherein the content of polyamide elastomer (A) is less than 1% by weight, the surface resistivity is high (no antistatic property). In the case of the thermoplastic resin composition of Comparative Example 24 wherein said content is more than 90% by weight, the flexural modulus of elasticity is low.

Table 6

	Example			
	22	23	24	25
Compounding recipe (Parts)				
(A) Component				
Polyamide elastomer PAE-A	13	-	13	13
PAE-B	-	13	-	-
(C) Component				
Styrene resin (2)-1	30	30	-	30
(2)-2	-	-	38	-
(2)-3	57	57	49	57
(B) (b) Component				
Reaction product b-1	5	5	5	1
b-2	-	-	-	-
b-3	-	-	-	-
b-4	-	-	-	-
b-5	-	-	-	-
b-6	-	-	-	-

- to be cont'd. -

Table 6 (Cont'd.)

26	27	28	29	30	31	32	33	34
13	13	5	30	13	13	13	13	13
-	-	-	-	-	-	-	-	-
30	30	46	10	30	30	30	30	30
-	-	-	-	-	-	-	-	-
57	57	49	60	57	57	57	57	57
10	30	5	5	-	-	-	-	-
-	-	-	-	5	-	-	-	-
-	-	-	-	-	5	-	-	-
-	-	-	-	-	-	5	-	-
-	-	-	-	-	-	-	5	-
-	-	-	-	-	-	-	-	5

- to be cont'd. -

Table 6 (Cont'd.)

Physical properties				
Melt flow rate (g/10 min)	22	15	32	23
Izod impact strength (Kg·cm/cm)	36	45	36	20
Heat distortion temperature (°C)	91	91	91	93
Flexural modulus (Kg/cm ²)	25,000	25,000	25,000	25,000
Tensile strength (Kg/cm ²)	420	400	420	400
Surface resistivity (after one day) (Ω)	1x10 ¹⁰	8x10 ¹¹	1x10 ¹⁰	5x10 ¹⁰
Surface resistivity (after being allowed to stand for one month and subsequently washed) (Ω)	1x10 ¹⁰	1x10 ¹²	1x10 ¹⁰	5x10 ¹⁰
Appearance (visual checking)	○	○	○	○

-to be cont'd. -

Table 6 (Cont'd.)

23	24	19	32	18	21	21	22	24
45	60	38	25	24	33	24	21	38
90	82	92	88	91	91	90	89	90
24,000	19,000	28,000	16,000	25,000	25,000	25,000	25,000	25,000
430	380	520	250	410	420	440	410	400
1×10^{10}	1×10^{10}	8×10^{11}	6×10^9	1×10^{10}	1×10^{10}	3×10^{10}	5×10^{10}	1×10^{10}
2×10^{10}	3×10^{10}	9×10^{11}	5×10^9	2×10^{10}	1×10^{10}	3×10^{10}	6×10^{10}	2×10^{10}
○	○	○	○	○	○	○	○	○

Table 6 (continued)

	Comparative Example			
	16	17	18	19
Compounding recipe (Parts)				
(A) Polyamide elastomer PAE-E	12	-	12	12
PAE-B	-	12	-	-
(C) Styrene resin (2)-1	30	30	-	26
(2)-2	-	-	38	-
(2)-3	58	58	50	58
(B) (b) Reaction product b-3	-	-	-	-
(B) (b) (2) Functional group- (2)-4 containing	-	-	-	4
styrene resin (2)-5	-	-	-	-

- to be cont'd. -

Table 6 (Cont'd.)

20	21	22	23	24	25
12	12	13	0.5	95	-
-	-	-	-	-	-
26	30	30	34	-	34
-	-	-	-	-	-
58	54	57	65.5	5	66
-	-	0.05	5	5	-
8	-	-	-	-	-
-	4	-	-	-	-

- to be cont'd. -

Table 6 (Cont'd.)

Physical properties				
Melt flow rate (g/10 min)	22	13	34	19
Izod impact resistance (Kg·cm/cm)	13	20	12	17
Heat distortion temperature (°C)	92	94	93	93
Flexural modulus (Kg/cm ²)	25,000	25,000	25,000	25,000
Tensile strength (Kg/cm ²)	400	400	400	410
Surface resistivity (after one day) (Ω)	1x10 ¹²	8x10 ¹³	2x10 ¹²	2x10 ¹⁰
Surface resistivity (after being allowed to stand for one month and subsequently washed) (Ω)	1x10 ¹²	9x10 ¹³	3x10 ¹²	2x10 ¹⁰
Appearance (visual checking)	○	○	○	△ silver

- to be cont'd. -

Table 6 (Cont'd.)

16	10	22	14	65	14
14	16	13	36	Not broken	34
93	93	93	93	45	93
25,000	25,000	25,000	29,000	3,000	29,000
420	420	400	400	130	410
2×10^{10}	2×10^{10}	2×10^{12}	$> 1 \times 10^{16}$	6×10^9	$> 1 \times 10^{16}$
2×10^{10}	3×10^{10}	3×10^{12}	$> 1 \times 10^{16}$	5×10^9	$> 1 \times 10^{16}$
X Silver Delustering	X Silver Delustering	○	○	○	○

Claims

1. A thermoplastic resin composition comprising

(A) 1-90% by weight of a polyamide elastomer and

(B) 99-10% by weight of at least one of the following (a) and (b):

(a) a rubber-modified thermoplastic styrene resin consisting of a rubber-modified styrene polymer containing a hydroxyl group-containing alkenyl monomer as a copolymerized component or a mixture of a rubber-modified styrene polymer with a styrene polymer, in which mixture at least one of these polymers contains a hydroxyl group-containing alkenyl monomer as a copolymerized component,

(b) a mixture or reaction product of (1) 40-99% by weight of a thermoplastic polyurethane with (2) 60-1% by weight of a functional group-containing styrene resin in which a styrene resin is copolymerized with an unsaturated compound having at least one functional group selected from the group consisting of a carboxyl group, an acid anhydride group, an amino group, an epoxy group and a hydroxyl group.

2. The thermoplastic resin composition according to Claim 1, wherein the polyamide elastomer (A) is a polyetheresteramide which is composed of (i) an aminocarboxylic acid or lactam having 6 or more carbon

atoms, or a nylon mn salt in which $m + n$ is 12 or more, (ii) a poly(ethylene oxide)glycol having a number-average molecular weight of 200-6,000 and (iii) a dicarboxylic acid having 4-20 carbon atoms and which contains a polyetherester unit in an amount of 10-95% by weight.

5 3. The thermoplastic resin composition according to Claim 1, wherein the (B) component is (a) a rubber-modified styrene thermoplastic resin which contains a hydroxyl group-containing alkenyl monomer as a copolymerized component in an amount of 0.01-15% by weight.

4. A thermoplastic resin composition according to Claim 1, wherein the (B) component is composed of (b)(1) a thermoplastic polyurethane and (b)(2) an aromatic alkenyl copolymer containing a functional group-containing styrene resin, the proportion of the (A) component to the (B)(b)(1) component is such that the
10 amount of the (A) component is 1-90% by weight and the amount of the (B)(b)(1) component is 99-10% by weight [(A) + (B)(b)(1) = 100% by weight], and the proportion of the aromatic alkenyl copolymer is 99-10% by weight per 1-90% by weight of the total of the (A) component and the (B)(b)(1) component [the total of the aromatic alkenyl copolymer, the (A) component and the (B)(b)(1) component is 100% by weight].

15 5. The thermoplastic resin composition according to Claim 1, wherein the (B) component is a reaction product obtained by reacting (b)(1) a thermoplastic polyurethane with (b)(2) a functional group-containing styrene resin under melt kneading; (C) a styrene resin is contained in an amount of 99-10% by weight per 1-90% by weight of the (A) component, and the proportion of the (B)(b) component is 0.1-50 parts by weight per 100 parts by weight of the total of the (A) component and the (C) component.
20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 89309082.9

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.) 5
P, X, Y	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 12, no. 410, October 28, 1988 THE PATENT OFFICE JAPANESE GOVERNMENT page 32 C 540 * Kokai-no. 63-146 956 (JAPAN SYNTHETIC RUBBER CO. LTD.) *	1, 3	C 08 L 77/00 C 08 L 77/12 C 08 L 51/06 C 08 L 55/02 C 08 L 75/04 C 08 L 25/08 C 08 L 25/10
D, Y	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 11, no. 96, March 26, 1987 THE PATENT OFFICE JAPANESE GOVERNMENT page 45 C 412 * Kokai-no. 61-246 244 (TORAY IND. INC.) *	1, 2	
Y	DE - A1 - 3 545 033 (EMS-INVENTA AG) * Claims * & GB-A-2 170 502	1, 4, 5	TECHNICAL FIELDS SEARCHED (Int. Cl.) 5 C 08 L 25/00 C 08 L 51/00 C 08 L 55/00
Y	US - A - 4 740 552 (GRANT et al.) * Claims *	1, 4, 5	C 08 L 75/00 C 08 L 77/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 07-12-1989	Examiner WEIGERSTORFER
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EP 0 form 1503 01 82